THE MANUFACTURE

OF EARTH COLOURS

DR JOSEF BERSCH

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PREFACE

ORIGINALLY issued as a volume of the series on pigments and colouring matters by the present author's father, the necessity for a new edition afforded a welcome opportunity of revising "*Earth Colours.*" Although, in the nature of things, little progress has been made in this subject itself, there was a good deal to add in connection with the mechanical appliances for treating the colour earths and manufacturing them into pigments. In other respects, too, the work has been carefully gone through and brought up to date, with new and additional illustrations.

The author desires to express his thanks to the various firms who have afforded him assistance in his task by furnishing illustrations and descriptions of new machinery, together with other information. It is hoped that this third edition will meet the approval of those interested in the subject ; and the author will be glad to receive supplementary information to render the work more complete in the event of a future edition being found advisable.

PROF. DR. WILHELM BERSCH.

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EARTH COLOURS

CHAPTER I

BOTH from the chemical and practical standpoint it is necessary to divide pigments into clearly defined groups, the following classification being adopted on the basis and natural history of the substances concerned :—

(1) Pigments occurring native in a finished condition, and only requiring mechanical preparation to fit them for use as painters' colours. (2) Pigments which are not ready formed in Nature, but contain some metallic compound as pigmentary material, which requires certain chemical treatment for its full development. (3) Pigments which, in contrast to these two groups, contain only organic, and no inorganic, constituents. This last class comprises all the natural vegetable pigments, together with the large group of colours obtained artificially from tar products, fresh groups of which are being continually introduced. Nowadays, there is no longer any strict line of demarcation between the natural and artificial organic colouring matters, it being possible to produce even those of the vegetable series, such as madder and indigo, by artificial means.

I

Whilst this group of colours exhibits the greatest variety, and is constantly being enriched and increased by the progress of colour chemistry, the case is different with the first group, the natural earth pigments. Here we have chiefly to do with the preparation of materials occurring in Nature, or with bringing about certain chemical results, so that, consequently, the range of variety is far more restricted, and there is little or no possibility of increasing the number of these colours by the manufacture of really new products. The earth colours nevertheless have a high technical and economic importance, on account of their extremely valuable properties, coupled, for the most part, with low cost.

If the term " earth colours " were. strictly adhered to, the present work would have to be confined to a description of the physical and chemical properties of the various pigments, and of the various means by which they can be brought into suitable condition for use in paints.

However, of late, the term has found wider application than formerly, since it has been found practicable to modify (shade) certain of the earth colours by simple operations, and thus considerably increase the range of tones of the substances known as earth colours. The progress of chemical industry has also largely increased the number of the so-called earth colours, certain methods of chemical treatment having enabled substances that are of little use for other purposes, to be employed, in large quantities, as pigments. The application of these—usually cheap—by-products is still further facilitated by the fact that they can be transformed, by a simple chemical treatment, into pigments which are distinguished by their beauty of

colour and at the same time possess the great advantages of durability and cheapness.

As an example of this, mention may be made of iron oxide, which occurs in Nature in the form of various minerals which can be made into pigments by mechanical treatment. In many cases, this treatment has already been carried out by Nature, and deposits of iron oxide are found in which the material has only to be incorporated with a vehicle to make it fit for immediate use as a painters' colour.

Moreover, the same oxide is obtained, in large quantities, as a by-product of the treatment of other minerals. From the point of view of chemical composition, this by-product is of very low value, by reason of the large supplies of native oxide available. By means of a very simple chemical treatment, however, this by-product oxide can be considerably improved in commercial value, being, in many cases, convertible, by merely heating it to certain temperatures, into a variety of colours which sell at remunerative prices.

Consequently, in view of the present condition of the chemical industry, the term " earth colours " can be enlarged to include a number of waste products which fetch good prices as colours, though otherwise practically valueless in themselves.

The number of earth pigments is very large, and comprises representatives of all the principal colours. For painting purposes, few pigments beyond the earth colours were known to the ancients; and most of the colours in the paintings which have come down to us from antiquity are pure earth pigments, thus affording proof of their great durability, having retained their freshness unimpaired for hundreds—and some for thousands—of years.

The earth colours might be divided into such as occur ready-formed in Nature, and require only mechanical preparation, and which either require special treatment (*e. g.* calcining), or are artificial products (like the iron oxide mentioned above). Since, however, such a classification would not advantage our knowledge of the nature of this class of colours, it appears useless and superfluous, and we will therefore simply confine ourselves to arranging the earth pigments according to their colour—white, yellow, red, etc.

Adopting this classification, the following minerals and chemical products may be considered as earth colours :—

White.—These include the varieties of calcium carbonate, such as chalk, marble, precipitated chalk, calcium phosphate, calcium sulphate (in the form of gypsum, alabaster, muriacite and the precipitated gypsum produced as a by-product in many chemical works), heavy spar, the different varieties of clay, and magnesia.

Yellow.—This group comprises ferric hydroxide (hydrated oxide of iron) in the form of the various minerals known as ochre ; all the preparations chiefly composed of this hydroxide, and all those prepared by artificial means. A very important member of this group is orpiment ; the other arsenical compounds frequently met with native, being however, on account of their poisonous properties, no longer used as pigments.

Red.—Chief among the red earth colours are those consisting of ferric oxide (iron oxide), under various names. The only other member of the group is the far rarer vermilion.

Blue.—The blue earth colours are few in number and of no particular beauty ; but they are of importance

on account of their cheapness and because all the artificial blue pigments are rather expensive. Two products in particular merit attention in this connection, namely, ultramarine, and the mineral known as blue ochre or blue ironstone. The latter, as a matter of fact, cannot be used for anything else than a painters' colour, and can be obtained at a low price; whereas ultramarine also forms a valuable raw material for the recovery of copper, and is therefore dearer.

Green.—This group, again, contains only two members, viz. malachite green (chrysocolla), and the green earths (seladonite), known as Verona, etc., green. These occur fairly often in Nature, and the green earths in particular find a wide industrial application by reason of their low price. Malachite green is very similar, in chemical constitution, to ultramarine; and both form sources of copper and are consequently expensive.

It should be mentioned that both ultramarine and malachite green can only be profitably made into pigments where the minerals can be obtained cheaply, since both of them can be manufactured where artificial pigments are produced, and are put on the market under the same names as the native articles. The very low price of the green earths makes them highly popular as colouring matters in certain branches of industry, and they are very largely used by wall-paper manufacturers.

Brown.—This is a large group, and the pigments composing it are specially distinguished for their beauty and depth of colour, on which account they are used in the finest paintings. Here, again, it is ferric oxide, in combination with water—and therefore ferric hydroxide—that furnishes a large number of the members of the group. Like the renowned Siena earth,

the artists' colours known as Vandyck brown, bole, Lemnos earth, umber, etc., mainly consist of more or less pure ferric hydroxide. These minerals are, moreover, specially important to the colour manufacturer, inasmuch as most of them enable a large number of different shades to be obtained by a simple method of treatment consisting merely of the application of heat in a suitable manner; and these colours are among the most excellent we possess, by reason of their beauty and permanence. Amongst this series must also be classed native manganese brown, which chiefly consists of a mixture of manganese oxide and the hydrated peroxide of the same metal.

Black.—There is really only one member of this class, which, however, is frequently used, viz. that form of carbon occurring as hexagonal crystals and known as graphite. Another natural black natural product, occasionally used as a painters' colour is the so-called black chalk. However, since black pigments can be produced very cheaply by artificial means, the natural colours find only a limited application; and only in one instance is graphite used alone, viz. for making blacklead pencils.

As already mentioned, certain chemical industries furnish by-products which are of very little value in themselves, and many of them, indeed, may be classed as worthless, since chemical manufacturers naturally endeavour to get everything possible out of their materials in the course of manufacture.

Some of these by-products, however, can advantageously be used as pigments, a good example of this being afforded by the iron oxide formed as a by-product in the manufacture of fuming sulphuric acid (Nordhausen oil of vitriol), by the old process, from green

vitriol (ferrous sulphate). In itself, this oxide is practically valueless, but, by very simple treatment, it can be converted into very valuable pigments which have a market value far in excess of the original material. Although it has hitherto been the custom to confine the term earth colours to such as occur ready-formed in Nature and only require simple mechanical treatment to make them ready for immediate use as pigments, the author is nevertheless of opinion that a book dealing exhaustively with earth colours should also make some mention of all the mineral colouring matters which can be easily made into pigments by simple processes, such as calcination or bringing into association with other substances. In accordance with this view, the present work will describe all the pigments that are obtainable in this manner. Most of the earth colours consist of decomposition products of certain minerals; and this applies particularly to such of them as contain iron oxide. According as the decomposition of the original mineral has been more or less extensive, the natural product exhibits different properties; and the manufacturer must consequently endeavour to treat them in such a manner as to ensure that the pigment obtained will be as uniform as possible in shade and permanence. In order to accomplish this it is essential to have an accurate knowledge of the origin of the raw material under treatment, and of its chemical and physical properties. In view of this, the author considers it necessary to deal more fully with the pigmentary earths forming the raw materials of the earth colours, before passing on to the preparation of the colours themselves.

CHAPTER II

THE RAW MATERIALS FOR EARTH COLOURS

THE minerals constituting the raw materials for the preparation of the earth colours occur under very divergent conditions in Nature. Some of them, such as chalk, form immense deposits, even whole mountains, whilst in other cases, *e. g.* the blue ferruginous earths, the occurrence is connected with certain local conditions, and many are found only in isolated deposits, as pockets or beds. This last is the case, for instance, with the handsome brown iron pigments; and indeed the names by which they are known indicate that they are only found in well-defined localities, or that they are met with of special quality there. The brown earth colour known to all painters as Terra di Siena, is found at many other places as well as near Siena, but the product from that city acquired aforetime a special reputation for beauty, and therefore all similar earths, provided they are equal to that from Siena, also bear the same name in commerce.

A number of raw materials for the preparation of earth colours are found, it is true, in many deposits, but their utilisation depends, in turn, on local conditions. For example, many copper mines contain, in addition to the other cupriferous minerals, those used, in the powdered state, as ultramarine or ultramarine green, and not infrequently lumps of mineral

are found containing both blue and green together. However, it is only when these minerals occur in sufficient quantity to make the necessary sorting profitable that their manufacture into pigments can be regarded as practicable.

Before commencing to work a deposit it is essential to make sure whether the raw material, or pigmentary earth, is actually suitable for the manufacture of earth colour. Even the general character of the material is important, those of soft, earthy consistency being much easier to treat, and the cost of preparation smaller, than if the raw material be hard, tough and crystalline.

The extent and thickness of the deposit, and the ease with which it can be worked, also play an important, and even decisive part, since, other conditions being equal, it will not pay to erect a colour works unless the raw material is available in sufficient quantity and is cheap. Generally, the deposit is not homogeneous throughout, the mineral being purer in some places and more contaminated with gangue in others. The percentage of moisture also varies, and in short, a number of circumstances must be taken into consideration in forming a conclusion as to whether a deposit is workable or not.

In order to arrive at a reliable opinion on all these conditions, sampling is indispensable. If the samples are of uniform character, they can be mixed together to make an average sample. But if they differ considerably in appearance, general character, proportion of gangue, etc., it is preferable to examine them separately, more especially when the area which each represents is large.

The examination should extend, on the one hand,

to the natural percentage of moisture, and, on the other, to the purity of the material. The water content is determined by thoroughly drying a weighed sample, bearing, however, in mind the fact that pigmentary earths of a clayey nature vary in water content according to the time of year, besides changing in accordance with the weather when the won material is stored in the open.

The purity can only be ascertained by an examination in which a sample of the soft, clayey material is crushed and passed through a narrow-mesh gauze sieve, the amount of the coarse particles—sand, small stones, etc.—remaining on the sieve being determined. A more accurate method, of course, is to separate the true pigmentary earth from the gangue by levigation. For this purpose, a weighed quantity of the crushed, air-dry sample is placed in a relatively narrow glass vessel and thoroughly mixed with water, the turbid supernatant liquid being poured off after a short interval. The residue is repeatedly treated in the same way, until no more fine particles remain in suspension, the residue then consisting of impurities, or gangue. Of course, the washings can be collected, the suspended matter allowed to settle, and finally weighed in an air-dry condition. By this means an approximate idea of the yield of earth colour can be obtained at the same time.

Raw materials which are not amorphous, soft and clayey must first be crushed, an operation facilitated by heating to redness and quenching in cold water. Oftentimes the heating causes a change of colour and improves the covering power—a point to which reference will be made later on.

In the following description of the various raw

materials, the chemical composition of the pure minerals will be given, together with an enumeration of the most common impurities.

(A) WHITE RAW MATERIALS AND PIGMENTARY EARTHS

Limestone (Calcite, Limestone, Chalk)

The number of materials furnishing white earth colours is comparatively large, and these colours are particularly important, because, not only are they extensively used by themselves, but they also serve as adjuncts to other colours and for the production of special shades. The chief raw material for the preparation of white earth colours is the mineral calcite in its numerous modifications.

Calcite, or calc spar, occurs very frequently in Nature, and is one of the most highly diversified minerals known. In its purest state it appears as " double spar " (calcite), in the form of water-white crystals, which are very remarkable for certain optical properties. White marble is also a very pure variety of calcite, in which the individual crystals are very small. The various coloured marbles owe their appearance to certain admixtures of extraneous substances, chiefly metallic oxides.

No sharp line of demarcation separates marble from ordinary limestone, the difference between them really consisting only in the degree of fineness of grain; and all limestones which grind and polish well may be classed as marble. As is the case with marble, there are also limestones of various colours, grey being, however, the most common. This grey limestone forms huge mountain masses which, in Europe, follow

for example, the Alpine chain on its northern and southern edges.

A few other examples of calcite may be mentioned which occur in certain localities and, in part, are still in course of formation. To these belong the stalactites and stalagmites, which sometimes consist of extremely pure calcite. They are formed by the action of water, containing carbonic acid in solution, which trickles through cracks and cavities in limestone rock and dissolves out calcium carbonate from the adjacent stone. On prolonged exposure to the air such water gives off its free carbonic acid again ; and as the calcium carbonate is insoluble in pure water, it separates out in crystalline form. The masses formed in this way usually resemble icicles in shape, and the finest examples are to be found in the well-known stalactite grottoes at Krain, whilst the grotto at Adelsberg is renowned for its beautiful stalactites. Occasionally, stalactites have an opaque yellow or brownish tinge, which they owe to the presence of iron oxide.

A formation similar in its origin to stalactites is the so-called calc sinter and calcareous tuff. The former often occurs in cavities as irregular masses which, in some places, enclose large quantities of fossil animal bones, in which case they form " bone breccia " (crag breccia). Calcareous tuff is deposited from numerous springs, occasionally in very large quantities, enveloping plants and sometimes forming thick deposits in which the structure of the plants can be clearly recognised.

In some places a more or less pure white, extremely friable variety of calcite is met with under the name " mountain milk " or " mountain chalk " (earthy calcite), which seems to be a decomposition product,

and consists of a mixture of arragonite and chalk. Arragonite—which will be referred to later—is completely identical, chemically, with calcite—both being composed of calcium carbonate—the sole difference being their crystalline form.

The most important for the colour-maker, however, is the variety known as chalk. This is really a fossil product, *i. e.* it consists of the microscopic shells of marine animals united into solid masses. Despite the smallness of these animals, their epoch lasted long enough for their shells to form entire mountains which are encountered all over the world. A large part of the coast of England, the island of Rügen, and many other localities, consist entirely of chalk.

In many cases, chalk is found interspersed with nodular masses of flint, and in some places it also contains great quantities of the remains of other marine animals, such as sea urchins, the spines of which occur in such numbers in certain kinds of chalk as to unfit them entirely for use as a pigment.

The foregoing varieties of calc spar are the most important, and also occur in large quantities; but, to complete the tale, it is necessary to mention also a few others which, however, are only found in small amounts. To these belong, for example, anthracolite, a limestone stained quite black by coal; the oolithic limestones or roe stones, which are composed of granules resembling fish roe; muschelkalk, which is also of fossil character and is almost entirely composed of mussel shells cemented together with lime; the marls, which consist of calc spar mixed with varying quantities of clay and consequently often bear a great resemblance to loam in their properties. A few of these varieties find extensive employment for certain purposes, some

marls for instance being used for making hydraulic lime, whilst all modifications of calc spar that are sufficiently pure can be burned for quick lime.

It has already been stated that the mineral arragonite is identical, chemically, with calc spar, since both consist of calcium carbonate, but differ in their crystalline habit. Thus, whereas the crystals of calc spar belong to the rhombohedral or hexagonal system, those of arragonite are always rhombic. This occurrence of one and the same substance in two different crystalline forms is known as dimorphism, and calcium carbonate is therefore dimorphous. Whether calcium carbonate assumes the form of calcite or arragonite depends entirely on physical causes. When the deposition of the carbonate takes place from a cold solution the shape of the crystals is always one belonging to the hexagonal or rhombohedral system; but when it is from hot solution, rhombic crystals are invariably formed, calc spar resulting in the former case and arragonite in the latter.

These different methods of formation which can be carried out in the laboratory by producing the requisite conditions, occur on the large scale in many parts of the world. Wherever a hot spring comes to the surface, containing considerable amounts of lime in solution, this separates out in the form of arragonite, which received its name from the circumstance that specially handsome crystals of this mineral are found in Arragon.

One of the best-known places where the formation of arragonite can be observed at the present time is Carlsbad in Bohemia. The hot springs there deposit a very large amount of lime, which is stained more or less yellow or red by the presence of varying quan-

tities of iron oxide, and, under the name of " sprudel-stein " is used for producing various works of art. When the hot springs bring up particles of sand, the lime substance incrusts these sand grains, forming globular masses resembling peas, and consequently named pisolite.

In chemical composition, calcite and arragonite consist of a combination of calcium oxide (lime) and carbonic acid, the formula being expressed by $CaCO_3$. Calcium carbonate is insoluble in pure water, but dissolves somewhat freely in water charged with free carbonic acid. It is assumed that a compound is formed, which is known as calcium bi- (or acid) car-bonate, is very unstable and can only exist in a state of solution. When a solution of calcium bicarbonate—which can be prepared by passing carbonic acid gas through water containing finely divided calcium carbonate in suspension—is exposed for some time to the air, it soon becomes cloudy, and a deposit of calcium carbonate settles down at the bottom of the vessel, because, in the air the dissolved calcium bicarbonate is decomposed into free carbonic acid gas and calcium carbonate, which latter, as has been mentioned, is quite insoluble in water. It has already been stated that this phenomenon goes on in Nature in the forma-tion of stalactites, lime sinter and calcareous tuff.

Calcium carbonate is readily soluble in acids, the contained carbonic acid being liberated (as carbon dioxide) with effervescence. When such acids are employed for solution as form readily soluble salts with lime, such as hydrochloric, nitric, acetic, etc. acids, a perfectly clear solution is obtained; but if sulphuric acid is used, a white pulpy mass is formed, consisting of calcium sulphate, or gypsum, which

owing to its low solubility, separates out as small crystals. Any sandy residue left when calcium carbonate is dissolved, mostly consists of quartz sand. In dissolving dark-coloured limestones, grey, or even black, flakes are left, which consist of organic material very high in carbon. On limestone being subjected to fairly strong calcination, all the carbonic acid is expelled, leaving behind the so-called quick or burnt lime, which is, chemically, calcium oxide :—

$$CaCO_3 = CaO + CO_2$$
$$\text{Calcium carbonate} = \text{Quick lime} + \text{Carbon dioxide}$$
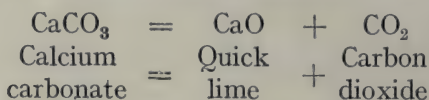
If burnt lime be left exposed to the air for some time, it again gradually absorbs carbon dioxide and is reconverted into calcium carbonate. When burnt lime is sprinkled with water it takes up the latter avidly, becoming very hot and finally crumbling down to a very friable white powder, consisting of slaked or hydrated lime (calcium hydroxide, $Ca(OH)_2$). The considerable rise of temperature in quenching the lime is due to the chemical combination of the calcium oxide and water.

Both quick and slaked lime dissolve to a certain extent in water, and impart strongly alkaline properties thereto, lime being one of the strongest of bases. On exposure to the air, the solution of quick lime in water (lime-water) quickly forms an opalescent superficial film of calcium carbonate, and in a short time no more lime is present in solution, the whole having been transformed into calcium carbonate, which settles down to the bottom of the vessel as a very fine powder.

Limestone that consists entirely of calcium oxide and carbon dioxide is of rare occurrence in Nature,

foreign substances being nearly always present. Since the nature of these admixtures is of the greatest importance to the colour-maker, owing to the considerable influence they exert on the suitability of the minerals for his purposes, it is necessary that these extraneous substances occurring in limestone should be more closely described.

Nearly all varieties of limestone contain certain proportions of ferrous and ferric oxides. The presence of ferrous oxide, when the relative amount is but small, cannot be detected by mere inspection; and even many limestones containing really appreciable quantities of ferrous oxide are pure white in colour so long as they are in large lumps. If, however, such a limestone be reduced to powder and exposed to the air for a short time, it gradually assumes a yellow tinge, the depth of which increases with the length of exposure.

The cause of this change is due to the fact that ferrous oxide has a great affinity for oxygen, by absorbing which it changes into ferric oxide. (Ferrous oxide consists of FeO, ferric oxide of Fe_2O_3.) Ferrous oxide and its compounds are of a pale green colour which is not very noticeable, whereas ferric oxide has a very powerful yellow colour, and consequently the limestone, when its superficial area has been greatly increased by reduction to powder, assumes the yellow tinge due to ferric oxide. A limestone exhibiting this property can evidently not be used for making white earth colours, but is, at best, only suitable for mixing with other colours.

Occasionally, limestone contains varying quantities of magnesia, and when this oxide is present in large amount, changes into another mineral known as

dolomite. In many places this dolomite forms large masses of rock, which, however, is not employed for making colours, owing to the yellow shade imparted by the fairly large amount of ferric oxide present.

Gypsum (Alabaster)

This mineral occurs native in many places, and is frequently worked for a number of purposes. Gypsum occurs in Nature in a great variety of forms. The purest kind is met with either as water-clear crystals, which cleave readily in two directions, or as transparent tabular masses (selenite) which also cleave easily. Micro-crystalline fine-grained gypsum is milk-white in colour, highly translucent and is largely used, under the name of alabaster, in sculpture. Owing to its low hardness, alabaster can be readily cut with a knife, and on this account is frequently shaped by planing or lathe-turning.

Gypsum is generally met with in dense masses, which may be of any colour, grey, blue and reddish shades being the most common, whilst pure white is rarer. The dark-coloured varieties can only be used for manurial purposes; but the white finds a two-fold application as a pigment, and, in the calcined state, for making plaster casts.

In point of chemical composition, gypsum consists of sulphate of lime, or calcium sulphate ($CaSO_4 + 2H_2O$). It is soluble in water, but only in such small quantity that over 400 parts of the latter are needed to dissolve one part of gypsum. On being heated to between $120°$ and $130°$ C., gypsum parts with its two molecules of combined water and becomes anhydrous calcium sulphate or burnt gypsum. When this latter is stirred with water to a pulp, it takes up the water again, with

considerable evolution of heat, swelling up considerably and setting quickly to a solid mass.

The number of substances exhibiting this property being small, burnt gypsum is very frequently used for making casts of statuary, and for stucco work in building. Finely ground white gypsum can also be used as a pigment, but is inferior to calcium carbonate in covering power, and is therefore seldom employed for this purpose, though frequently added to other colours. The mineral known as muriacite or anhydrite consists of anhydrous calcium sulphate; and is therefore similar in composition to burnt gypsum; but it lacks the property of combining with water when brought into contact therewith.

Barytes, or Heavy Spar

The mineral known as heavy spar occurs in very large quantities and in numerous localities. It forms rhombic crystals, which are very often extremely well developed and form flat plates of considerable size. A remarkable peculiarity of this mineral is its high specific gravity, which is due to the barium content. It is found native in all colours, white being the most common.

Chemically, heavy spar is barium sulphate, $BaSO_4$. It can be used as a pigment *per se*, but only when prepared artificially, the trade name for the product being permanent white, or blanc fixe. Powdered native heavy spar, even when ground ever so fine, has not enough covering power, this property being peculiar to the artificial product.

When it is desired to mix other pigments with a white substance, to lighten the shade, permanent white can be specially recommended, since it is quite

insensitive to atmospheric influences and has no chemical action on the colour, so that it can be used with even the most delicate colours without risk. In this way, not only can the colours be considerably cheapened, but over-dark colours can be shaded to the desired extent. Another advantage of such mixtures is that a smaller quantity of oil or varnish is required, barytes only needing about 8% of its own weight of vehicle to form a workable mixture, whilst other pigments take five times as much, or even more. In many cases the low covering power of barytes enables large quantities to be added, and this reacts favourably on the consumption of varnish.

Another barium mineral is witherite, or barium carbonate. This is not used direct as a pigment, but—in contrast to heavy spar—is readily soluble in hydrochloric acid, and therefore serves as raw material for the preparation of artificial barytes and other barium compounds, the first-named being obtained by treating a solution of barium chloride with sulphuric acid, insoluble barium sulphate being precipitated.

Talc, Soapstone, Steatite

Talc occurs in Nature either as a pure white mass, of greasy lustre, or occasionally as yellow, green or grey masses, all distinguished by a peculiar greasy appearance and a soapy feel. This appearance is common to all the minerals of the steatite group, and is the cause of their generic name, soapstone. Although the steatites have a very low degree of hardness— most of them can be scratched by the finger-nail— some difficulty is encountered in reducing them to fine powder. Calcination usually increases the hardness considerably, so that, in some cases, the calcined

mineral gives off sparks when struck with a steel instrument.

Soapstone is composed of magnesium silicates, containing varying proportions of magnesia and silica, together with a small quantity of water, apparently in a state of chemical combination, a very high temperature, approaching white heat, being required to effect its complete expulsion, the residue then attaining the aforesaid high degree of hardness. The composition of talc can be expressed by the symbol $H_2Mg_2(SiO_3)_4$, corresponding to 63·52% of silica, 31·72% of magnesia, and 4·76% of water. In some varieties of talc, a portion (1–5%) of the magnesia is replaced by ferrous oxide. Talc is quite unaffected by the action of dilute acids, boiling concentrated sulphuric acid being required to decompose it, with separation of silica.

Owing to its low specific gravity and chemical indifference, talc is suitable for lightening the shade of certain lake pigments. It can also be used as a pigment by itself, and also as a gloss on wall-paper, for mixing with paper pulp, and for various other purposes.

Clay

The mineral known as clay is, in all cases, a product of the decomposition of other minerals, mainly felspar. This substance is a double silicate of alumina and potash, $K_2O.Al_2O_3.(SiO_2)_6$. Pure kaolin is $Al_2O_3(SiO_2)_2 + 2H_2O$, or 46·50% silica, 39·56% alumina, 13·9% water.

Clay may be supposed to have been formed by the conversion of felspar, under the action of air and water, into silicate of alumina, the silicate of potash being dissolved out. Being insoluble, the silicate of alumina would be transported by the water, in a very fine

state of division, and finally deposited as a sediment, which in course of time became a solid mass. This, when again brought into contact with water, forms a very plastic pulp which, when dried and baked, forms a solid mass, brick, which is no longer affected by water. Perfectly pure clay forms a white mass, which, under the name of China clay or kaolin, is used for making porcelain, and is only occasionally met with in large quantities.

Pure kaolin is characterised by its great chemical indifference, being decomposed only by strong alkalis and sulphuric acid. At the high temperature of the pottery kiln, kaolin sinters to a very compact mass, but cannot be fused, except when small quantities are subjected to the intense heat of the oxyhydrogen flame, whereupon it fuses to a colourless glass of great hardness.

In an impure state, silicate of alumina occurs frequently in Nature, and then forms the minerals known under the generic names of clay, loam, marl, etc. These impure clays contain varying proportions of extraneous minerals which produce changes in the physical and chemical properties. They are grey, blue or yellow in colour, the grey and blue varieties mostly containing appreciable quantities of ferrous oxide, whilst the yellow kinds contain ferric oxide. When fired, all of them become yellow or red, the ferrous oxide being transformed into ferric oxide by the heat. Some fairly white clays are high in lime, which makes them fusible at high temperatures. In some very impure kinds, even the comparatively low heat of the brick-kiln is sufficient to cause partial fusion. For colour-making, the white clays, especially kaolin and pipeclay, form a highly important material,

being procurable at very low prices and fairly easy to prepare.

The white clays are either used as pigments by themselves, or for mixing with other colours of low specific gravity.

(B) Yellow Earths

The number of yellow earths is large, but most of them exhibit a certain similarity in chemical composition, the pigmentary principle in the majority being either ferric oxide or ferric hydroxide. The former is yellow, the latter brown, and the colour of the minerals resembles that of the preponderating iron compound.

Brown Ironstone

The mineral known as brown ironstone consists of ferric hydroxide, and usually forms compact masses, no decided crystals having, so far, been observed. The lumps have an irregular or earthy fracture, a hardness of 5–5·5, and a sp. gr. between 3·40 and 3·95. The colour ranges, in the different varieties, from yellowish (rusty) brown, through cinnamon to blackish-brown. The chemical composition of the pure lumps may be expressed by the symbol $2Fe_2O_3 + 3H_2O$; but a little manganese oxide and silica is generally present even in the pure kinds.

The chief varieties of this mineral are :—

(a) Fibrous brown iron ore, or brown hematite, mostly forming reniform or stalactitic masses.

(b) Compact brown ironstone, usually in dense masses, and not infrequently also appearing in pseudomorphs of other minerals.

(c) Ochreous brown ironstone. This variety is the most important to the colour-maker, for whose purposes

it is preferably used. It nearly always forms very loose, earthy masses, yellow or brown in colour.

(d) Clay ironstone. This consists of a mixture of the above-mentioned varieties with variable proportions of other minerals, clay being the most common ingredient. Nodular iron ore, oölitic, bog and siliceous ore belong to this class, as also the minette ores that are found in great abundance in Alsace-Lorraine, Belgium and Luxemburg, and are classed with the oölitic brown ironstones.

In most cases, the varieties enumerated are found together, and are used for the production of iron. The ochre constituting the most interesting member to the colour-maker often occurs as deposits embedded in dense masses of brown ironstone, though in many places it is found by itself.

CHEMICAL COMPOSITION OF VARIOUS BROWN IRONSTONES

The following analyses of brown ironstone from different deposits will give an idea of the composition of these minerals.

Ordinary Brown Ironstone

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Ferric oxide	76.76	73.75	77.54	78.50	78.42	48.25	—	—	—	—
Manganese oxide	16.56	10.50	2.70	1.95	1.30	24.73	—	—	—	—
Iron	—	—	—	—	—	—	33.9	37.88	54.80	55.04
Manganese	—	—	—	—	—	—	0.15	0.17	0.57	0.20
Alumina	—	—	—	—	1.13	2.33	10.03	0.88	1.15	2.50
Lime	0.60	2.75	0.48	5.08	3.55	2.85	0.41	0.32	0.50	0.34
Magnesia	6.44	—	1.25	4.50	0.18	0.90	0.67	—	0.02	0.38
Silica	—	—	3.55	0.85	5.48	11.35	28.29	33.38	0.02	0.38
SO_3	—	—	—	—	—	0.09	—	—	—	—
P_2O_5	—	—	—	—	0.09	0.08	—	—	—	—
Sulphur	—	—	—	—	—	—	0.33	0.06	0.04	Trace
Phosphorus	—	—	—	—	—	—	0.04	0.56	0.02	0.06
Loss on incineration	5.65	14.00	14.51	9.12	9.10	9.80	9.88	7.77	10.55	10.71

Deposits: (1) Hamm; (2) Schmalkalden; (3) Hüttenberg (Carynthia); (4) Styria; (5) and (9) Bilbao; (6) Algeria; (7) Schwelm (Westphalia); (8) Elbingerode (Harz); (10) Pennsylvania.

Argillaceous Brown Ironstone

	a.	b.	c.	d.	e.	f.	g.	h.	i.	k.
Ferric oxide	80·76	19·4	55·39	66·33	57·32	52·50	39·50	75·67	—	—
Iron	—	—	—	—	—	—	—	—	40·90	21·69
Manganese oxide	—	8·2	—	6·42	—	5·49	6·12	0·72	—	—
Manganese	—	—	—	—	—	—	—	—	—	—
Zinc oxide	0·92	1·6	—	—	0·47	—	—	—	—	—
Alumina	2·36	11·0	12·80	7·74	1·68	5·23	9·89	3·10	4·95	3·88
Lime	—	2·6	Trace	0·41	0·13	3·36	20·34	5·01	5·59	21·25
Magnesia	—	0·2	—	0·37	—	0·36	—	—	0·49	0·30
Silica	4·58	48·61	22·73	12·97	30·64	8·64	5·22	8·70	16·63	14·71
P_2O_5	—	—	—	—	0·32	3·86	2·19	3·68	—	—
Phosphorus	—	—	—	0·02	—	—	—	—	1·13	0·48
SO_3	—	—	—	0·03	Trace	—	—	—	—	—
Sulphur	—	—	—	—	—	—	—	—	0·10	0·05
Loss on incineration	12·71	9·1	8·50	11·77	12·70	20·55	25·74	—	16·04	28·70

(a) Oölitic (pea) ore from Elligserbrick (Brunswick); (b) from Durlach (Baden); (c) and (d) Ore from Esslingen; (e) Oölitic ore from Siptingen (Baden); (f) from Adenstedt, nr. Pirna (argillaceous); (g) *Ibid.* (calcareous); (h) Minette from Esch; (i) Red minette from Dolvaux; (k) Brown minette from Redange.

Limonite (Bog Iron Ore)

	1.	2.	3.	4.	5.	6.
Ferric oxide	61·00	67·46	65·66	67·59	70·05	62·20
Manganese oxide	7·00	3·19	3·87	1·45	1·78	7·60
P_2O_5	2·00	0·67	1·13	0·18	0·34	1·60
SO_3	—	3·07	Trace	0·21	Trace	Trace
Silica	6·00	7·00	7·15	7·89	8·03	16·60
Alumina	—	—	5·09	4·18	1·50	2·20
Lime	—	0·90	0·82	0·47	2·31	1·60
Magnesia	—	—	0·15	0·23	0·12	3·73
Water and organic acids	19·00	17·00	16·22	17·81	15·87	19·90

(1) Limonite from Lausitz; (2) Limonite from Auer, nr. Morizburg; (3 to 6) Swedish limonite.

Ochre

Ochre, or yellow Terra di Siena, forms earthy-looking masses, fawn, reddish-yellow to brownish-red in colour. Whilst not infrequent in Nature, ochre is only found in small quantities, as pockets, and not as extensive deposits. The discovery of a bed of good

coloured ochre is, however, always a very valuable find, bright natural ochres being somewhat rare, and most kinds requiring special preparation before they can be used as painters' colours. Owing to the comparative scarcity of good coloured ochres, they are often called after the place of origin, such as Thuringian, Italian (Siena), English, etc., ochre.

In nearly every case, ochre is a decomposition product of various ferruginous minerals, which has been transported by water, often in admixture with other minerals, and finally deposited in the places where it is now found. Most ochres consist of varying mixtures of clay, ferric hydroxide and lime; and, as a rule, the higher the proportion of ferric hydroxide, the deeper the colour. Thus, for example, the ferric hydroxide may amount, in the dark grades, to 25% of the entire mass, whilst in the lighter kinds it may be as low as 3%. It is very rare that ochre is put on the market in its native condition, being mostly subjected to chemical treatment enabling a definite shade of colour to be obtained. This will be gone into more fully later.

Yellow Earth

Yellow earth is found in many places as compact masses, and less frequently as schistous deposits. It has a fine earthy fracture, and is mostly devoid of lustre, except for a faint shimmer on the surface of fracture; slightly greasy feel; and a tendency to crumble, in water, to a non-plastic powder. It contains silica, ferric oxide and water in varying proportions, and the yellow earths from different deposits always vary slightly in percentage composition. These differences are clearly shown in the following analyses

of two varieties from the vicinity of Amberg (Bavaria) :—

					I.	II.
Silica	.	.	.	.	33·23%	35·10%
Alumina	.	.	.	.	14·21	14·40
Magnesia	.	.	.	.	1·38	—
Ferric oxide	.	.	.	.	37·76	36·80
Water	.	.	.	.	13·24	13·60

When heated, the colour changes gradually to red, and the earth becomes extremely hard. There are several recognised commercial grades, the price of which varies mainly in accordance with the colour and fineness. The Amberg variety is specially esteemed, the Hungarian and Moravian kinds being less valuable.

The colour not being particularly good, this earth is never used for fine work, but is largely employed as a yellow wash for houses and as ordinary distemper. It may also be used as an oil paint.

Red Ochre is a less important, cheap variety of ochre, chiefly used in cheap paints and for low-priced wall-papers. It occurs in the deposits as clayey masses.

Terra di Siena

Terra di Siena is a very pure form of ferric hydroxide. When ground, the light to dark brown lumps furnish a pale to dark yellow powder, which can be transformed into a number of gradations by burning. In spite of its handsome colour, this pigment is deficient in covering power, in addition to which it darkens when mixed with varnish, and dries slowly.

(C) The Red Earths

Apart from the small quantities of native vermilion handsome enough for direct use as painters' colours.

when reduced to powder, the red earths, with practically no exception, consist of ferruginous minerals, and it is only within a recent period that red painters' colours have been prepared from certain chemical waste products from manufacturing processes. In all cases, however, compounds of iron and oxygen constitute the bulk of the red earths. In addition to ferric oxide, which is the chief material used for making the important red colours, are compounds of ferric oxide and water, *i. e.* ferric hydroxides. The ferric oxide pigments are among the most important in the entire series of earth colours, being on the one hand very cheap, and on the other so handsome in colour that ferric oxide can be used for the finest paintings.

Ferric oxide can also be shaded very extensively by a fairly simple treatment, so as to furnish a whole range of very handsome shades.

In nature, ferric oxide occurs in numerous varieties of one and the same mineral, red iron ore, which is also known as hematite, blood stone, raddle, etc.

Red Ironstone

Red hematite occurs native as rhombohedral crystals, which mostly consist solely of ferric oxide, and may be considered as pure oxide for the purposes of the colour-maker. The difference between the several varieties is due, not to any chemical variation, but entirely to changes in physical structure. The varieties with a radial, fibrous structure are known as red hematite, the colour of which ranges from blood red to dark brown and is frequently accompanied by metallic lustre. The scaly modification of this mineral forms micaceous iron ore, and is usually a deep iron black.

In the neighbourhood of volcanoes it is frequently found as particularly handsome crystals.

Iron cream (frosty hematite) is the name given to a beautiful cherry red variety, which easily rubs off, has a greasy feel and is composed of extremely fine scales.

The so-called raddle occurs in Nature as a readily pulverulent earthy mass of ferric oxide contaminated more or less with extraneous substances. On account of its abundance and low market price, it is largely used in painting.

Although mixed with numerous foreign substances, certain clay ironstones, oölitic ironstones and siliceous ironstones may be regarded as ferric oxide in the sense understood by the colour-maker, all these minerals having a deep red to deep brown colour and being capable of finding advantageous employment as pigments.

Ferric oxide is distinguished by two properties which render it specially valuable to the colour-maker. When combined with water, its colour is no longer red, but a handsome brown; and, on the other hand, when heated, the colour passes through brown into a permanent dark violet. By suitable treatment of such minerals as consist mainly of ferric hydroxide, mixtures can be obtained which contain the oxide and hydroxide in variable proportions and give a whole range of shades between brown and red.

The preparation of these colours is easy when very pure red ironstone is available. The somewhat expensive pigment, Indian red, is—when pure—really nothing but a very pure ferric oxide of Indian origin. Ferric oxide, however, often contains impurities which considerably influence the colour of the product.

Owing to the fact that large quantities of ferric oxide are formed as by-products in certain chemical processes which are carried out on a very extensive scale, this oxide, which is very pure, can be advantageously used for making iron pigments, especially as its application for other purposes is very restricted, and it can therefore be had at a very low price.

The following analyses show the composition of a number of red ironstones, Nos. 1, 2 and 3 being hematite from Froment, or Wetzlar, No 4 from Wetzlar, Nos. 5 and 6 hematite from Whitehaven, No. 7 from Thuringia, No. 8 from Bohemia, No. 9 from Spain, No. 10 from N. America, and No. 11 from England.

No.	Ferric oxide.	Manganese oxide.	Silica.	P_2O_5.	Alumina, lime and magnesia.	Water.
1	94·00	Trace	2·00	—	Trace	2·00
2	80·95	—	16·74	0·51	0·97	0·83
3	73·77	—	23·16	0·45	1·41	1·21
4	92·45	—	5·63	0·19	0·65	1·08
5	96·27	—	4·20	—	0·59	4·40
6	63·05	5·29	22·76	—	0·49	4·40
7	85·00	1·601	3·304	0·457	8·795	0·633

No.	Iron.	Man-ganese.	Alu-mina.	Lime.	Mag-nesia.	Silica.	Sulphur.	Phos-phorus.	Loss on calcina-tion.
8	33·64	0·10	7·58	8·10	0·82	17·80	Trace	0·19	9·82
9	31·38	0·19	0·06	29·95	0·35	0·87	—	0·09	23·68
10	62·54	1·93	1·71	—	0·50	3·80	0·02	0·04	2·23
11	62·91	Trace	1·39	0·70	0·42	5·89	0·05	0·11	—

There are certain other minerals closely allied, both chemically and mineralogically, to red ironstone, namely, the brown hematites or ironstones used in the

manufacture of iron. Brown hematite consists of ferric hydroxide, $Fe_2O_3H_2O$, and occurs in a variety of forms in Nature, the most frequent being pea (oölitic) ore, which owes its name to the spherical shape of the grains. Some brown hematites are decomposition products of other minerals, and contain sulphur and phosphorus in addition to ferric hydroxide. Like the pure hydroxide, they are brown in colour, but differ therefrom considerably in their chemical behaviour when heated. This is particularly the case with the so-called bog ore, which is mostly found, as spongy yellow-brown to black masses, in swamps, and owes its origin to the decomposition of various ferruginous minerals. It varies greatly in chemical composition and occasionally contains up to about 50% of sand. The amount of ferric oxide in bog ore varies between 20 and 60%, and it also contains 7–30% of water, up to 4% of P_2O_5, small quantities of ferrous oxide and manganese hydroxide, together with, in most cases, mechanically admixed organic residues.

The phosphorus content makes bog iron a very inferior material for smelting, the resulting iron being of low quality. Nevertheless, it can sometimes be advantageously used in making earth colours, though the products cannot lay much claim to beauty of colour.

Bole

The native earth pigments known by this name form masses of the colour of leather to dark brown, with a conchoidal fracture and an earthy appearance. Bole chiefly consists of iron silicate combined with water, some varieties containing small quantities of alumina. The composition fluctuates very considerably,

most varieties containing 41–42% of silica, 20–25% of alumina, and 24–25% of water, the remainder consisting of ferric oxide. Some kinds, such as Oravicza and Sinope bole, contain only 31–32% of silica and 17–21% of water.

Bole is used as a paint for walls, clapboards, etc., and is only mentioned here because of its relationship to the ferric oxide pigments.

Alum Sludge

Large quantities of clarification sludge are produced, in alum works, as the sediment from the red liquors. This sludge consists mainly of ferric oxide, with small quantities of other oxides and sulphuric acid (basic ferric sulphate, and would be an entirely worthless by-product except for the fact that it can be manufactured into pigments, some of them of great beauty.

All alum makers should treat this residue and convert it into pigments, which they could put on the market at a low rate, the cost of preparation being small. Since the material is chiefly composed of ferric oxide, the resulting colours are very similar to those obtained from iron ores; and all shades, from yellow-brown, through red, to the darkest brown, are represented.

Mine Sludge

The water frequently present in iron mines sometimes contains large quantities of sediment, which consist mainly of iron ochre and can be advantageously worked up into pigments. There is scarcely any need to mention that all substances containing ferric oxide can be used for making any of the pigments obtainable from the oxide itself, the only difference

between the various raw materials being their degree of purity, so that it is not always so easy to obtain a certain desired shade from a given material in such beauty as is furnished by another material, the small quantities of impurities associated with the ferric oxide having, in many instances, an important influence on the colour.

(D) BLUE EARTHS

Only two minerals are known which are capable of direct use as blue pigments, viz. vivianite (native Prussian blue) and copper carbonate (azurite, ultramarine), and as neither of them is particularly handsome, they are only used for unimportant work. Lapis lazuli is no longer employed.

Azurite, or Ultramarine

This mineral, which is of frequent occurrence with malachite and other cupriferous minerals, forms small crystals of a beautiful deep azure blue consisting of cupric oxide in combination with carbon dioxide and water, expressed by the formula $2CuCO_3,Cu(OH)_2$, or $Cu_3(OH)_2(CO_3)_2$, and containing 69.19% of cupric oxide, 25.58% of CO_2 and 5.23% of water. The colour of the powdered mineral is much paler than that of the crystals. The pigment, which is used for cheap paints, is not particularly stable, and loses much of its beauty when applied to plaster.

Vivianite

This mineral occurs in many places as crystalline masses, but also forms earthy deposits, some of which, especially in certain bogs, attain considerable thickness.

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The colour is between indigo and blackish blue; and the freshly won mineral often has an unsightly whitish appearance, which, however, soon changes into the pure blue. The cause of this peculiarity is due to the fact that vivianite originally consisted of hydrated ferrous phosphate, which is white, this compound being transformed, under the influence of the air, into the blue ferric phosphate.

Vivianite contains ferric oxide, phosphoric acid and water, but in variable proportions. The original composition, expressed by $Fe_2(PO_4)_2 + 8H_2O_2$, corresponds to 43·03% of ferrous oxide, 28·29% of P_2O_5 and 28·68% of water; but, in the air, part of the ferrous phosphate is oxidised to basic ferric phosphate, so that the content of ferrous oxide may range from 9·75 to 42·71%, and that of ferric oxide between 1·12 and 38·20%. Vivianite is also sold as blue ochre, and is now seldom used as a painters' colour, owing to the introduction of a large number of artificially prepared blues, which are superior to vivianite in colour and are cheaply made. However, it can still find application in localities where it is obtainable in quantity.

(E) Green Earth Pigments

The green earth pigments comprise green earth (Verona green) and malachite. Like the blue earths, they cannot lay any particular claim to beauty, but they are very cheap, and consequently are largely used where low price is the chief consideration.

Green Earth

In Nature, green occurs as an entirely non-crystalline earthy mass, which is probably a decomposition

product of augite. It has a close, earthy fracture, a colour between seladon and olive green, and a slightly greasy appearance. In point of chemical composition it consists of silica, alumina, magnesia, sodium, potassium, ferrous oxide and water, the usual representative formula being $ROS_1O_2\ H_2O$, in which RO symbolises a metallic oxide.

The colour is due to ferrous oxide ; and if left exposed to the air for a long time, or subjected to powerful calcination, the great affinity of ferrous oxide for oxygen causes the colour to turn red and red-brown.

Green earth is found in many localities, *e. g.* Bohemia, Hungary, the Tyrol and Cyprus, the finest, however, occurring near Verona, on which account it is known as Veronese earth.

Malachite

The commercial pigment consists of powdered malachite, a mineral which usually occurs in compact masses of a handsome emerald green colour, though isolated lumps exhibit considerable variation in shade, some of them being dark green and others very pale. In chemical composition, malachite is closely allied to azurite, consisting of cupric oxide, carbon dioxide and water, and the difference is entirely one of percentage proportions. The formula is $CuCO_3, Cu(OH)_2$, or $Cu_2(OH)_2CO_3$, corresponding to $71 \cdot 90\%$ of cupric oxide, $19 \cdot 94\%$ of carbon dioxide and $8 \cdot 16\%$ of water.

Powdered malachite (even the dark green varieties) is always rather light in colour, and for this reason is not much used. Furthermore, the mineral is rather hard ($3 \cdot 5$), and is consequently difficult to grind ; in addition to which the mineral is fairly expensive, on account of its employment as a source of copper,

particularly fine pieces being also used as ornaments or for making works of art. Moreover, like all copper compounds, it is very sensitive to the action of sulphuretted hydrogen, and liable to discoloration in course of time.

(F) Brown Earth Pigments

Numerous minerals are adapted for the manufacture of brown pigments. On the basis of chemical composition, they may be classed in two groups; those consisting of ferric hydroxide, and those in which the brown colour is due to organic substances.

The first group comprises the minerals which have already been mentioned in connection with the red earth pigments, bole and brown ochre (umber), Terra di Siena, Cologne earth and a number of other earths rich in ferric hydroxide belonging to this category. The second, or organic group, includes compounds that are very rich in carbon and are therefore of a very dark colour, the shades ranging from light brown to black, *e. g.* the true umbers and asphaltum.

Umber

As already mentioned, the term "umber" was formerly applied to brown varieties of ochre, whereas at present it is extended to certain masses of brown-coal character, often interspersed with iron ochre and sometimes containing manganese. Umber generally consists of fairly dense, earthy masses, which are dried and ground—after crushing and levigation, if necessary.

Valuable varieties are Cappagh brown and Caledonian brown, both with a reddish tinge.

It is thus evident that "umber" now implies two different kinds of materials, organic masses and iron-manganese compounds, which can also be used as oil paints. These umbers can also be extensively shaded by burning, the final colour being particularly influenced by the amount of manganese compounds present.

The carbonaceous umbers (Cassel brown, Carbon brown) are combustible, and mostly leave behind a merely small residue of ash. An important property of these umbers is their partial solubility in alkalis, a peculiarity which is utilised for the preparation of brown wood stains.

Asphaltum

Asphaltum forms very friable dark brown to black masses, which, in contact with a light, easily ignite and burn with a bright, but very smoky, flame, disengaging a peculiar, "bituminous" smell, and leaving only a very small quantity of ash.

Extensive deposits of asphaltum are found at the Dead Sea, the Pitch Lake on the island of Trinidad, in Dalmatia, and many other places, where, however, it is in an impure condition and frequently contains large quantities of sand. In many localities the rock is impregnated with asphaltum, which makes it dark brown to black in colour and gives rise to a bituminous odour when rubbed.

Peat beds sometimes contain pockets of a mass with a handsome brown colour and consisting of a mixture of humic acids and other organic substances which may be ranked with the humin bodies that are always formed when organic matter decomposes in presence of an insufficient supply of oxygen. These bodies are dark coloured, mostly deep brown, rich in carbon,

and, to some extent, similar to brown coal or peat in chemical composition.

Their high carbon content renders these substances very inert towards chemical reagents, and therefore particularly adapted for the preparation of painters' colours. Genuine Vandyke brown, which is the handsomest brown known, is an earth rich in humin compounds; and Cassel brown also belongs to this group.

(G) Black Earth

The colour of these earths is entirely due to carbon, and pure carbon, a certain form of which occurs native, is itself used as a pigment. Actually, there are only two minerals that require to be mentioned in this connection : black schist and graphite.

Black Schist

In most cases this is a clay shale, so rich in carbon as to appear deep black. In commerce, this mineral is also erroneously called " black chalk "; but at present it is seldom used as a pigment or drawing-material, black chalks being produced far more cheaply than the expense of preparing the natural article.

Grey clay shales are used for making grey earth pigments (stone grey, and mineral grey).

Graphite

This mineral is found, in a very pure state, in many localities, celebrated deposits occurring in England, Siberia, Bohemia and Bavaria, whilst North American graphite has lately come into prominence.

Graphite is a modification of pure carbon, and is

met with in the form of hexagonal (rhombohedral) crystals, usually occurring as hexagonal plates with a lustrous, iron-black colour. It rubs off easily, and readily burns away, leaving a very small amount of ash, when subjected to a very high temperature in presence of air.

The principal uses of graphite are as an anticorrosive paint for iron, and for making lead pencils.

As already mentioned, the term " earth colours " has been considerably broadened of late. Whereas, formerly, it was restricted to colours prepared exclusively from minerals by a simple treatment, limited to crushing, levigation or calcination, it now includes the pigments obtainable from large by-products of certain chemical processes. This latter class is especially important as affording an opportunity of utilising products formerly considered worthless and whose removal often entailed heavy expense.

By drawing on these materials the industry of the earth colours has greatly enlarged its scope. At present, many colours of this kind are on the market, and it is to the interest of many manufacturers to endeavour to utilise certain waste products in the same direction. The advantage of such a course hardly needs emphasising; but, to give only a single example, it may be mentioned that the manufacture of fuming sulphuric acid from green vitriol, by the old process, produces residues which were formerly looked upon as quite worthless, and sold at very low prices, but are now worked up, in a number of factories, into very handsome and durable pigments.

CHAPTER III

THE PREPARATION OF THE COLOUR EARTHS

THE preparation of the raw materials for the purpose of making earth colours is a very important matter, because many minerals or pigmentary earths merely require mechanical treatment to render them at once fit for use. The mechanical preparation differs considerably, in accordance with the raw material under treatment, substances that are found native in a finely powdered condition only needing, for the most part, to be levigated.

It rarely happens, however, that the raw material occurs in condition for use direct, an example of this kind being afforded by the finest clays or ochres. Whilst these are found in a state of extremely fine powder, they nearly always contain certain quantities of sandy ingredients or even large lumps of foreign minerals, and therefore require levigating. Sometimes they need crushing as well, the small particles cohering so strongly that mere treatment with water (levigation) is unable to separate them. Mechanical force is therefore necessary, a passage through grooved rollers being generally sufficient to crush the lumps; but in some cases stamps have to be used.

When solid materials have to be treated, mechanical appliances must always be used, their selection depending on the materials in question. Thus, gypsum, for

example, can be crushed with ordinary rolls or mill stones, its degree of hardness being so very low (2) that it can be scratched with the finger-nail.

If, however, the material to be reduced is limestone, which belongs to the third degree of the scale of hardness (can only be scratched with an iron nail), or heavy spar (hardness 3–3·5), very powerful stamps or edge-runners must be employed to break it down into small lumps, which can then be further reduced, without any special difficulty, in an ordinary mill.

It is thus evident that a great variety of mechanical appliances are used in the manufacture of earth colours. Before going into their construction it is necessary to point out that, whatever the mechanical treatment employed, a considerable expenditure of mechanical force is entailed; and more power is needed when mixtures have to be prepared. It is therefore essential, in planning a factory for making earth colours on a large scale, to make provision for ample motive power.

This power may be supplied by a steam engine; but it must not be forgotten that the prime cost and running expenses of such an engine are considerable, and form an important item in view of the low value of most earth colours. Consequently, it is highly important to be able to generate motive power as cheaply as possible.

Now, the cheapest and most uniform source of power is water; and therefore, wherever the conditions allow of the erection of the colour works near a stream or river, which can supply the power to run the various machinery, the most favourable circumstances will have been secured, the power being obtained at minimum cost, whilst the upkeep of the motor cannot be very great. If there is sufficient head for the water

to be run through a trough over the top of the levigation tanks, the conditions will be ideally favourable.

Wind power costs nothing, once the motor has been installed; but unfortunately, one is dependent on the weather, and sometimes there is not enough wind, for days together, to drive the sails at all, and therefore all the operations have to be stopped, including levigation, the water for which has to be raised by a windmill pump.

In districts where the winters are severe, water power may also fail and work have to be stopped; and consequently, even when water power is the prime source of energy, a steam engine must be installed as a stand-by, being, of course, only used when the main source of power gives out or proves insufficient.

The machines employed for preparing the raw materials in the manufacture of earth colours may be divided into the following groups :—

Machines operating entirely by pressure : crushers ; machines acting by impact : stamps ; those acting by impact and pressure : vertical mills (edge-runners), ball mills, centrifugal mills ; and, finally, machines with a frictional action : grinding mills. Then there are the levigating machines, which do not reduce the material but separate the coarser particles from the finer. The construction of the foregoing machines is a matter for the machinery manufacturer rather than the maker of earth colours ; but as the business of the latter is dependent on them, a short description is considered necessary. The selection depends, on the one hand, on the nature of the materials to be treated, and, on the other, on the size of the works, since a manufacturer who has to deal with large quantities of a given raw material will require different

machines from those used on a small scale. The sole purpose of the following description is to indicate to the colour maker the way in which the reduction of the raw material can be accomplished.

CRUSHING MACHINERY

Crushers and Breakers.—Crushers usually consist of grooved iron rollers revolving on horizontal axes. One of the rollers is fixed, the other being adjustable by screws, in order that lumps of different sizes may be treated in one and the same machine, which may be employed either to turn out a roughly crushed product, or to reduce it to a certain degree of fineness.

If several pairs of crushing rollers be mounted in series, and each set a little closer than its predecessor, the material can be reduced progressively from large lumps to a fairly fine powder.

Each pair of rollers is geared together by pinions, and is turned in such a way as to draw the material in between. If the gear pinions have the same number of teeth, the two rollers will revolve at the same speed and will then merely crush the material into lumps of a size depending on the distance at which the rollers are set apart.

Nevertheless, by simply altering the gear ratio of the pinions, the crushing action of the rollers can be supplemented by a grinding action, a much finer powder being then obtainable than otherwise, the one roller running at a higher speed than the other.

These crushers differ in strength of construction, very strongly built machines being required for dealing with large lumps of hard material, whereas substances of low crushing strength, such as clay or other earthy

materials, can be treated in much lighter machines.
In any case, however, it is advisable to have the machine
stronger than is absolutely necessary for the work in
view; for, although the prime cost is thus increased,
the outlay on repairs will be reduced, and the machines
can, if necessary, be used on harder material as well.
The framework supporting the rollers should always
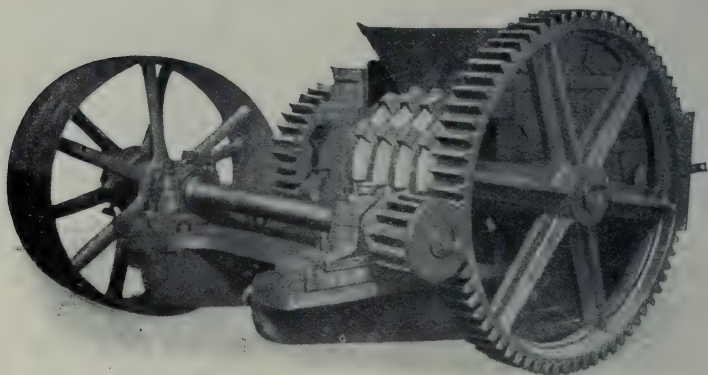consist of a strong iron casting; and the machine

FIG. 1.

should be set up as close as possible to the engine or
motor, to minimise the loss of power in transmission
through long shafting, etc.

Fig. 1 represents a breaker (made by the Badische
Maschinenfabrik, Durlach), suitable for the rough
crushing of clayey materials supplied in large lumps.
It can, however, also crush shale, lime, chalk, as well
as hard, sticky masses which would clog up a stone-
breaker.

The material fed into this breaker is gripped at once

by the powerful projecting teeth, which are connected together by sharp-edged ridges, and is crushed in such a way that it can be easily reduced still further by a succeeding pair of smooth rollers.

The granulator (Fig. 2), made by the same firm, is an example of a machine for crushing harder materials.
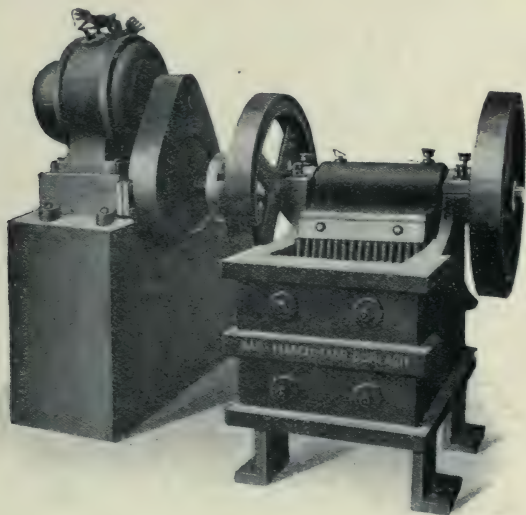
FIG. 2.

It is similar in construction to a stone-breaker, but differs in the movement of the jaws, and combines the properties of breaker and grinder, inasmuch as it tears the material as well as crushes it. The figure shows the machine adapted for direct electric drive. If necessary, these granulators can be fitted with classifying jig screens.

Stamps.—Stamps or stamping-mills have been used

from prehistoric times, and were probably employed for reducing hard materials long before the introduction of grinding-mills. The underlying principle of the stamping-mill is very simple. The material to be reduced is placed in a trough or mortar, and the ram or head, which is of considerable weight, is raised by a mechanical device and then allowed to fall freely, from a certain height, on to the material underneath, which it crushes. The heavier the head and the greater the height of fall, the greater the effect produced. As a rule, a large number of stamps are mounted together, and in such a way that half of them are being lifted while the other half are falling. Either a separate mortar or trough is arranged under each stamp, or else the whole drop into a common trough charged with the material under treatment. Sometimes a lateral movement is imparted to the material in the trough, so as to bring it under the action of all the stamps in succession.

Although the construction of stamping-mills in general appears simple, various modifications are employed for different purposes.

As a rule, a single passage through a stamping-mill is not sufficient to reduce the material completely to the desired fineness, the first product always containing large and coarse fragments of various sizes, as well as fine powder.

If the latter were left in with the larger pieces for the second stamping it would impede the work, and the stamping-mill should therefore be provided with means for classifying the material discharged from the trough, to separate the fine from the coarse and grade the latter into sizes. This is usually effected by means of a grading-screen.

Stamping-mills are chiefly used for reducing brittle materials. A number of stamps arranged in a row are alternately lifted, by means of cams mounted on a common shaft, and then let fall on to the material lying on a solid plate, or else on a grating through which
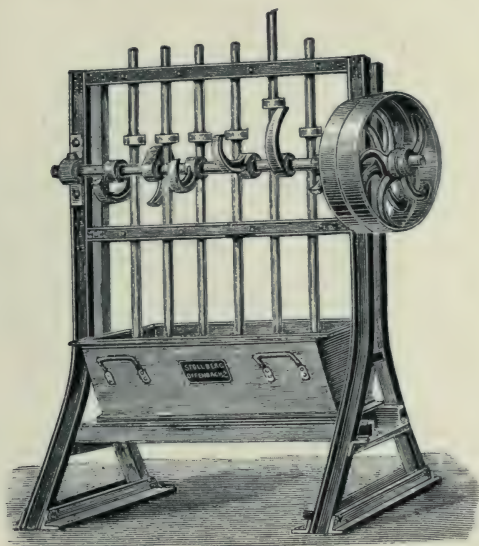

Fig. 3.

the crushings fall. Fig. 3 is a stamping-mill constructed by H. F. Stollberg, Offenbach.

These mills are very strongly built, as independent units, the frame being of cast-iron and the rams of best wrought-iron with interchangeable chill-cast heads. In some mills the stamps are rotated during the upstroke, in order to equalise the wear on the heads, and also to economise power.

The grating or trough holding the material is per-
forated with holes, the diameter of which varies with
the material under treatment and the desired degree
of fineness in the product. To increase the efficiency
of the mill, the grating or trough is adapted to move
while the mill is running, in order to clean itself auto-
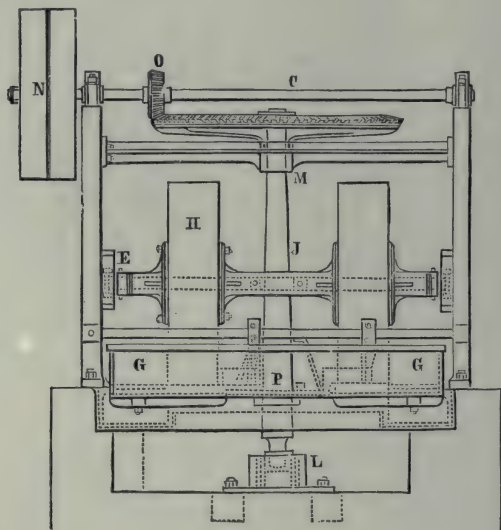
Fig. 4.

matically. These mills are made in different sizes,
with 2, 4, 6, or 8 heads.

Edge-runners.—This type of crusher is highly suitable
for reducing earth colours in large works. The special
feature of the type is that both stones are mounted
vertically and turn on a common shaft in the same way
that a cart wheel does on its axle. These runners are
particularly useful for reducing clay, chalk and other
earth colours, which have to be dealt with in large

quantities. They will also crush fairly large lumps, and they can therefore be used for the further reduction of materials roughly crushed in a breaker, etc. The material may be treated in either the wet or dry state, only slight alteration being needed to change from one method to the other.

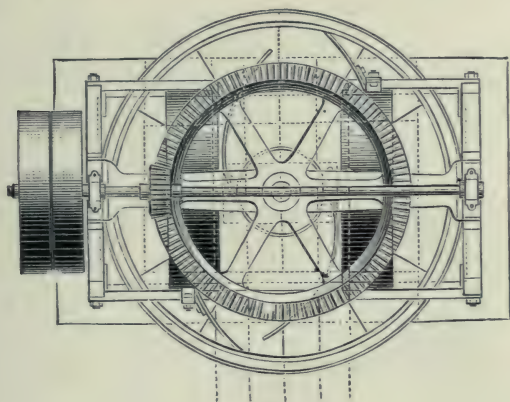There are numerous different patterns of edge-runner,

FIG. 5.

but all of them can be divided into two groups, viz. : mills with stationary troughs, whilst the shaft carrying the runners rotates; and those in which the trough revolves, and the stones merely turn on the stationary horizontal shaft.

Comparison of the efficiency of the two types has shown that the revolving-trough type is the better, giving a larger output per unit time with a reduced consumption of power. Figs. 4 and 5 show a vertical section and plan respectively of this type of edge-runner. The trough G is turned by means of a toothed crown

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gearing with the bevel pinion O mounted on an overhead shaft C driven by a belt pulley N.

The bearings of the vertical shaft J of the trough are situated at L and M. The runners H are loosely mounted on the fixed horizontal shaft E and revolve in consequence of the friction between them and the material in the trough. As the latter revolves, the material is continuously pushed aside by the runners, and is again brought under them by the action of scrapers.

The great advantages afforded by edge-runners, in consequence of their simplicity, easy management and low wear in comparison with other grinding appliances, have led to their reintroduction on a large scale. It should, however, be borne in mind that the edge-runner mill must be of a pattern suitable to the materials it will have to treat. The method of drive usually depends on local conditions. The revolving-trough type is chiefly useful for mixing, on account of the ease with which the materials can be charged.

The capacity of edge-runner mills depends on the nature of the material, the diameter and weight of the runners, the speed at which they are run, and also on the rate at which the reduced material is discharged in order to give place to fresh portions of the charge. This is effected by means of two sets of scrapers, the individual members of which can be adjusted in any direction. Their ploughing action also greatly assists the mixing effect.

Fig. 6 illustrates an edge-runner mill with revolving trough and overhead drive; and Fig. 7 one with stationary trough and bottom drive; both made by the Badische Maschinenfabrik, Durlach. The runners are of grey cast-iron, chill-castings or cast-steel being

used for crushing hard materials. The trough in all cases is lined with detachable chill-cast plates. Special attention is bestowed on the lubrication of all the moving parts, and all the lubricators are easily accessible.

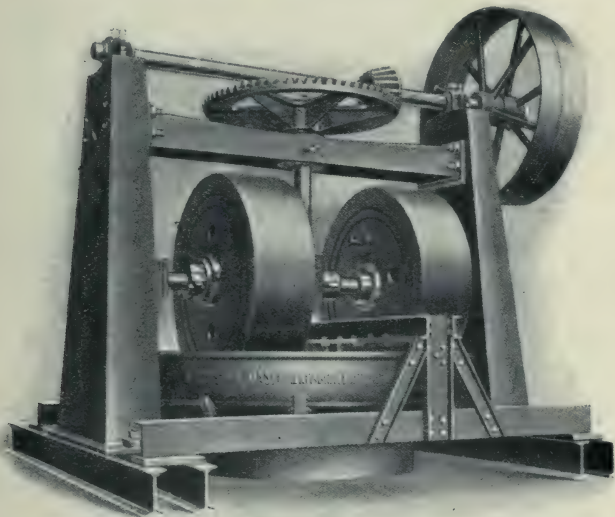The main shafts of the fixed-trough machines have

FIG. 6.

forged cranks, and the metal crank bearings are provided with dust caps. All the shaft journals run in detachable metal bushes.

A special advantage attaching to this type is the automatic screening device and the returning of the screen residue. In some cases, complicated appliances are employed to return the coarse residue from the screen, bucket elevators, worm conveyors, etc., all

entailing increased motive power, not inconsiderable wear, and a higher prime cost; but in this instance the object is achieved, without extra power or wear, by very simple means. The dust-proof shell enclosing the runners and screen is provided with large doors and charging hoppers.
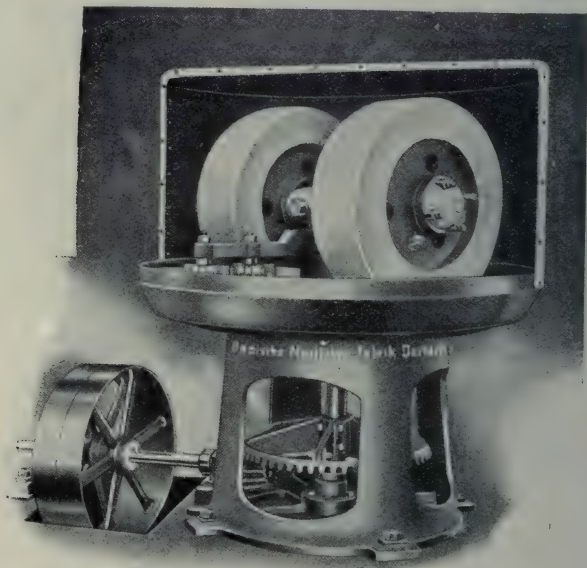

FIG. 7.

The motive power required to drive edge-runner mills depends on the dimensions of the mill and on the class of material to be treated; the larger the mill and the coarser the material, the more power needed to drive it.

This type is the more suitable for raw materials that are of an earthy character, so that all that is
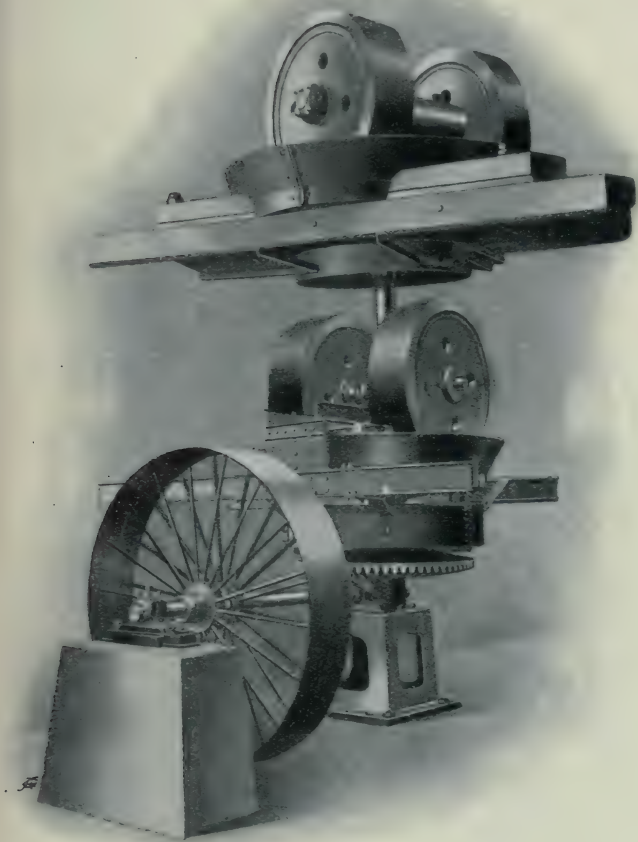
Fig. 8.

necessary is to destroy the cohesion of the particles, as is the case, for example, with clay and all earthy minerals.

The wet method of crushing with edge runners is

FIG. 9.

particularly suitable as a preliminary to levigation. A machine arranged for this purpose is shown in Fig. 8. It consists of two sets of edge runners, one with fixed, and the other with revolving trough. The material is introduced by hand, or by suitable charging mechan-

ism, into the upper, fixed-trough machine, where it is continuously sprinkled with water and kneaded by the one runner, and is passed thence to the second roller which forces it through the slotted bed into the bed of the lower set.   The slotted beds of the upper and
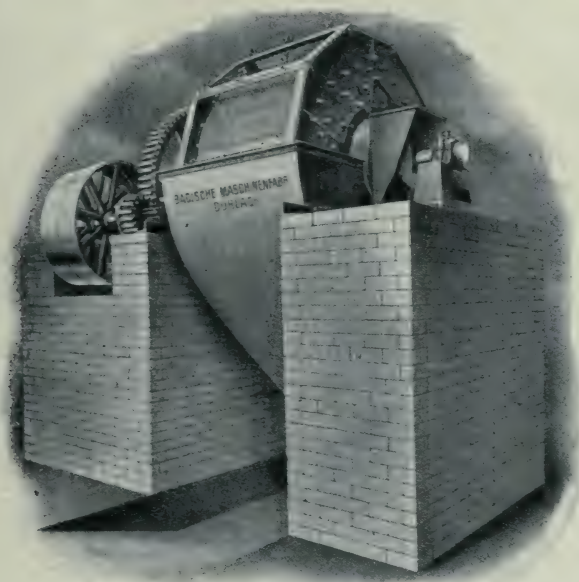

FIG. 10.

lower set are offset ; and the chief function of the lower set, with rotating bed, is to secure intimate admixture of the material which, in most cases, is already sufficiently reduced.

Ball Mills.—Ball mills are generally used for crushing dry materials to fine powder. The mill shown in Fig. 9 is a typical form of grinding drum enclosed in

a dust-proof casing, the latter being provided, at the top, with an opening connected to the dust exhaust pipe. The discharge outlet at the bottom can be closed by a slide.

The drum is provided with two strong lateral shields or cheeks (Fig. 10), one of which carries the interchangeable cross-arm and the charging hopper. Both cheeks are lined with detachable chill-cast plates, to take up the wear. The bed is formed of heavy steel bars (which can be turned round), between which are arranged adjustable slits for the discharge of the reduced material. Guard sieves are mounted all round, and close to, the bed, and interchangeable fine screens surround these in turn. The mesh of the fine screens determines the fineness of the product, and the residue falls down on to a plate which returns it to the interior of the drum. The reduction of the charge is effected by a number of very hard, forged steel balls of various sizes.

The mill must be run in the direction marked by the arrow on the outer shell, so that the residue on the screens can be returned to the drum by the plate provided for that purpose; and the prescribed working speed must be maintained. The mill must not be overloaded. The impact of the balls should be mild, but distinctly audible. Overloading reduces the output. Idle running causes the most wear, since the balls then roll directly on the bed, which, of course, should be prevented as far as possible. The feed is continuous; and, of course, only dry material should be introduced.

When the balls have lost size and weight through wear, they must be replaced by a fresh set.

Pulverisers.—Pulverisers are the best form of crusher

for tough and not over-hard materials. They are simple and strong in construction, of high capacity with comparatively small consumption of power, and furnish a good, uniform product, the size of
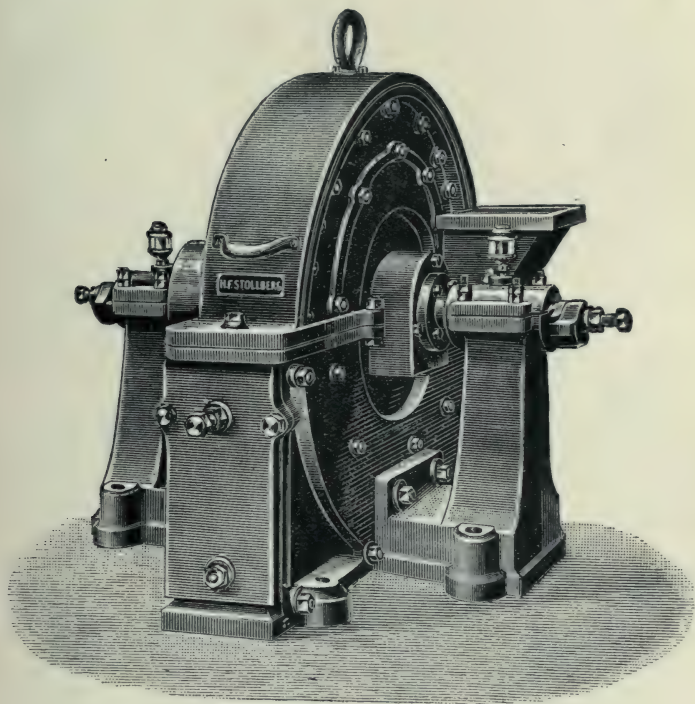

FIG. 11.

which ranges from fine powder to coarse granules, according to the screens used and the class of material treated.

The crushing is effected by a cross-arm beater, composed of four to six radial steel arms on a divided,

cast-steel hub, keyed on to the horizontal shaft. The arms are hardened, and are adjustably and detachably mounted on the hub.

The beating action of the arms, which run at high speed, forces the material against the studded surface of the hardened cheeks of the machine and also against the hardened square steel bars forming the periphery, the repeated impact of the material on itself, as well as against the arms and bars, progressively reducing it until small enough to fall through the screen on the under half of the casing, into a closed receptacle below. The screen mesh varies according to the degree of fineness required.

The peripheral bars are mounted in a very simple manner, and in such a way that when one edge of the bars is worn, a quarter turn brings a fresh, sharp edge into operation, so that all four edges of each bar can be utilised.

To prevent the escape of dust, the machine is provided with an air-circulation chamber, which maintains the flow of air in continuous circulation, the resulting strong draught also drawing the fine material through the screen and keeping the meshes open. By this means the capacity of the pulveriser is considerably increased. The interchange of the crushing organs and screens, and also the cleaning of the machine, can be effected without difficulty or loss of time.

The charge is introduced through a feed hopper at the side, and may vary, according to the size of the machine, from nut size to lumps twice as large as a man's fist. If necessary, suitable mechanical feed devices can be applied.

Disintegrators (Figs. 12 and 13).—This type of machine is used for reducing medium-hard or soft materials,

especially where it is desired to obtain a comparatively large output of a gritty product.

In the patterns shown, the main shaft is of steel, with dust- and dirt-proof red-brass bearings with pad or ring lubrication. The spindle case draws out to facilitate cleaning. Mechanical feeding attachments can be provided.
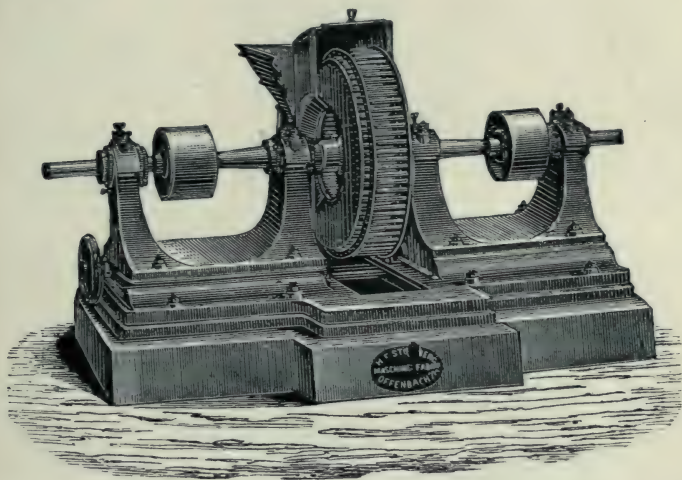

FIG. 12.

According to local conditions, the disintegrator can be mounted either on a brick foundation, with lateral discharge outlet into a storage bin, or on a raised grating of iron joists.

If the product is to be conveyed to a distance, it is advisable to have a hopper-shaped collector leading directly to a worm conveyor or bucket elevator.

The arrangement shown in Fig. 13, in which the disintegrator is mounted on a dust-proof cast-iron

collector, has been found very suitable for colour works
of various kinds (aniline, lead, mineral and other
colours), particularly on account of the suppression
of dust; whilst the automatic charging worm greatly
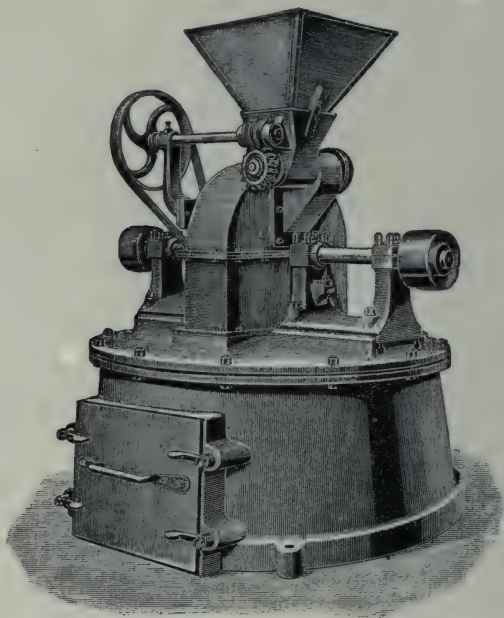increases the capacity as compared with charging by
hand.

FIG. 13.

LEVIGATION

The effect of levigation is based on the circumstance
that bodies of greater density than water remain longer
in suspension in that medium in proportion as the
fineness of their particles increases. This treatment
consequently enables the finer portions of a substance

to be mechanically separated from the coarser. Levigation is extensively practised in colour works because it furnishes powder of finer grain than can be obtained by even the most careful grinding.

The appliances used for levigation may be of a very simple character, consisting only of several tubs or tanks, mounted in such a way that the liquid contained in one can be run off into the one next below. With this primitive plant, the material to be levigated is stirred up in the water in the uppermost tub and left to settle until the coarsest particles may be assumed to have settled down, whereupon the turbid water is drawn off into another tub, in which it is left to settle completely. When the clear liquid has been carefully drawn off, a fine sludge is left in the bottom of the tub, consisting of the fine particles of material mixed with water.

When a particularly fine powder is required, a single levigation does not always suffice, but the liquid in the second tub must be left to settle for a short time only, and then run into a third for complete subsidence.

A well-designed levigator for treating large quantities of powder is illustrated in Fig. 14. A stirrer R, driven by cone gearing, is arranged in a wooden or stone vat G. The levigating water enters close to the bottom of the vat, through the pipe W. When G is half full of water, the stirrer is set running, and the substance to be levigated is added. After a while, the water laden with the levigated powder begins to run off at A into the long narrow trough T_1 provided, at the opposite end from A, with a number of perforations through which the water runs into the trough T_2. From this it escapes through the perforations into the trough T_3.

and thence successively into T_4 and T_5, finally discharging into the large tank S.

The coarsest and heaviest of the water-borne particles deposit in the trough T_1, finer particles settling down in T_2, and so on in succession, until the water reaching the tank S contains only the very finest of all in sus-
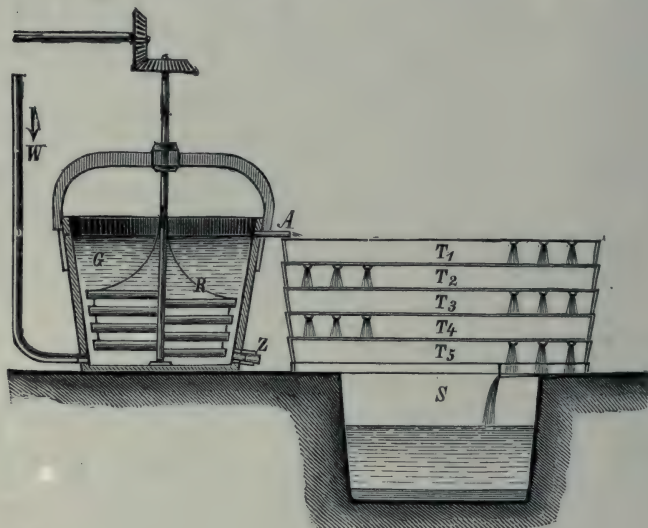

FIG. 14.

pension, these taking a long time to settle down to the bottom. The deposit in the upper troughs can be returned to the vat, whilst that in the lower ones will be fine enough to dry as it is. The residue in the vat is discharged through Z when the operation is finished.

It will be evident that the fineness of the product depends on the number and length of the troughs T, the larger these factors the more delicate will be the

particles remaining in prolonged suspension in the liquid.

Many earth colours require no treatment beyond levigation to fit them for use in paints. This is the case with, *e. g.*, the white clays; and certain grades of ferric oxide, which occur native in the state of fine powder, may also be included in this category. In many cases, however, if large quantities of a finely pulverulent mineral be stirred up with water and left to stand, the deposited solid matter forms such a highly coherent mass that it can only be distributed in water with difficulty, the fine particles adhering so firmly together that it is hardly possible to stir them up again completely in the liquid by means of a paddle.

Nevertheless, this can be easily effected by using a special appliance of the kind employed by starch manufacturers for a similar purpose, viz. the levigation of starch. This apparatus is designed in such a way that the pulpy charge of material is gradually and completely disseminated in the introduced liquid.

Fig. 15 shows a device of this kind, consisting of a circular vessel provided with a step bearing for a vertical shaft driven by cone pinions. The lower part of the shaft is provided with a thread, on which a nut is adapted to travel up and down. By means of rods, this nut is connected to a wooden cross-bar provided with stiff bristles on its lower face. A horizontal handle is attached to the nut. The water is admitted through the pipe on the right.

In working the apparatus, the shaft is rotated and the handle held firmly, thus causing the nut and attached cross-bar to rise to the limit of its travel. The levigating liquid, mixed with the material under treatment, is then admitted, until the vessel is full,

and when the solids have completely subsided, the clear liquid is drawn off, and the operation is repeated until a thick layer of sediment has accumulated on the bottom of the vessel.

To levigate this, the cross-arm carrying the bristles is lowered until it just touches the surface of the deposit, and a continuous stream of water is admitted through
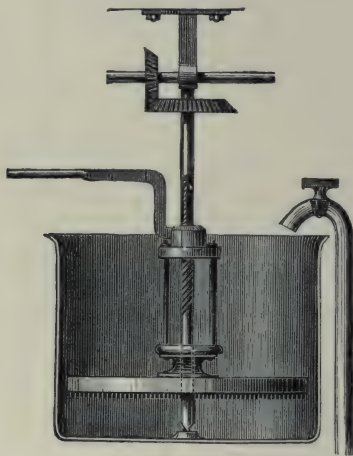

FIG. 15.

the pipe at the side. The bristles gradually disseminate the upper layers of the sediment in the water, which becomes turbid and is then drawn off into another vessel, cement-lined pits being used in the case of large quantities. When the brushes no longer encounter any of the sludge, the cross-arm is lowered sufficiently to stir up another layer; and in this way, large quantities of solid matter can be distributed in water. If the cross-arm is rotated at low enough speed, the

coarser particles of material keep on settling down again, and the collecting vessels will receive only the finest particles.

In addition to the mechanical separation of coarse and fine particles, levigation accomplishes another purpose, namely that the prolonged contact of the treated material with water dissolves out any admixed soluble constituents which might affect the quality of the colour, the latter being left in a purified condition.

For successful levigation it is essential that the charge should be in a sufficiently fine condition at the outset. Clayey raw materials require no preliminary treatment other, perhaps, than passing them through a disintegrator, whereas hard, crystalline substances must first be ground in a wet mill, such as an edge-runner mill with stationary bed, into which the materials are fed with an admixture of water, provision being made for keeping the charge under the runners all the time. The crushed material is screened previous to levigation.

In the levigation process a few vessels of large size are preferable to a number of small ones. The nature of the material will determine whether any stirrers are required or not, these being unnecessary in the case of the pigmentary earths, which naturally remain a long time in suspension and therefore do not require stirring up.

The pulpy levigated material is taken out of the tubs, etc., drained (if necessary) and dried. The draining may be effected in bags, or—in large plants—filter presses or hydro-extractors. In these latter instances, pumps will be provided for feeding the sludge direct to the presses, and conveyors for delivering the pressed material to the drying-plant.

5

Draining and Drying

The levigated colour earths form a stiff pulp containing a large quantity of water, which can be eliminated in various ways. Usually, the mass is dried by spreading it out thinly on boards and leaving it exposed to the air until it has become solid; or else it is only left long enough to acquire the consistence of a thick paste, which is then shaped into cones or blocks, which are allowed to dry completely in an airy place. If the colours are to be sold in the form of powder, the dried lumps are crushed.

To accelerate drying, the pulp may be put through a hydro-extractor, or dried in hot-air stoves or rooms. As, however, this last method entails special appliances and also expenditure, this acceleration is only resorted to when rendered necessary by special conditions.

The Hydro-extractor.—When a substance is set in rapid rotation, it tends to fly away from the centre at which the rotational force is applied. The centrifugal force thus coming into action increases with the velocity of rotation and with the distance of the substance from the axis of rotation.

The centrifugal hydro-extractor consists, therefore, of a vessel in rapid rotation; and if a liquid be introduced into such vessel, it is projected with considerable force against the peripheral walls. If the peripheral surface be perforated, the liquid portion of a charge consisting of liquid and solid matters will be ejected through the perforations, while the solid matter remains inside. As a rule, a few minutes' treatment in a hydro-extractor is sufficient to separate the water from a thin pulp so completely that the solid residue is in an almost completely dry state. A hydro-extractor which,

though of an old pattern, is well adapted for the purposes of the colour-maker, is shown in Fig. 16.

The drum A, which revolves easily on a vertical axis, is of metal, and is provided with a large number of fine perforations on its peripheral surface. It can be rotated at high speed by means of the crank f and
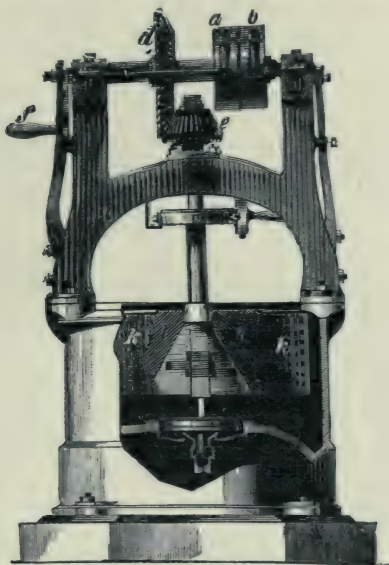

FIG. 16.

pinions d, e, or by the fast-and-loose pulley a b connected with a source of power. To prevent any of the charge from being projected over the rim of the drum, the upper edge is turned over so as to leave only a comparatively small opening at the top. The lower end of the drum shaft carries a strong steel spindle, which must be carefully machined and enable the drum to revolve as easily as possible. This is

essential, because even small machines require a comparatively large amount of motive power—which is not surprising in view of the high speed at which the drum has to revolve in order to perform its functions.

The drum is enclosed in a casing of somewhat larger diameter, which may be of any convenient material. The bottom of the casing is preferably tapered slightly downward, and is covered, at its lowest part—below the bearing of the drum—with a sieve communicating with a pipe through which the ejected liquid is drained off.

When a liquid, containing solid matter, is fed into the drum, which is already running at high speed, the liquid is thrown, by the centrifugal force, against the peripheral surface of the drum and escapes through the perforations, leaving the solid matter behind. Where large crystals are in question, as for instance in sugar factories, the centrifugal machine can be employed without any additional precautions, the liquid being expelled and the crystals being practically dried by keeping the machine running a short time longer. In the case of the pulp obtained by levigating colours, however, this procedure would result in failure, because the fine solid particles would be ejected along with the liquid and the drum would be left quite empty.

In this case it is therefore necessary to provide means for retaining the solid matter in the drum, and allow only the water to escape, with which object the drum is lined with a bag of closely woven fabric, open at the top and fitting snugly against the inner surface of the drum. When the drum is first started, the ejected liquid is milky, no fabric being sufficiently close to retain all the extremely fine solid particles present. In a very short time, however, the liquid will begin
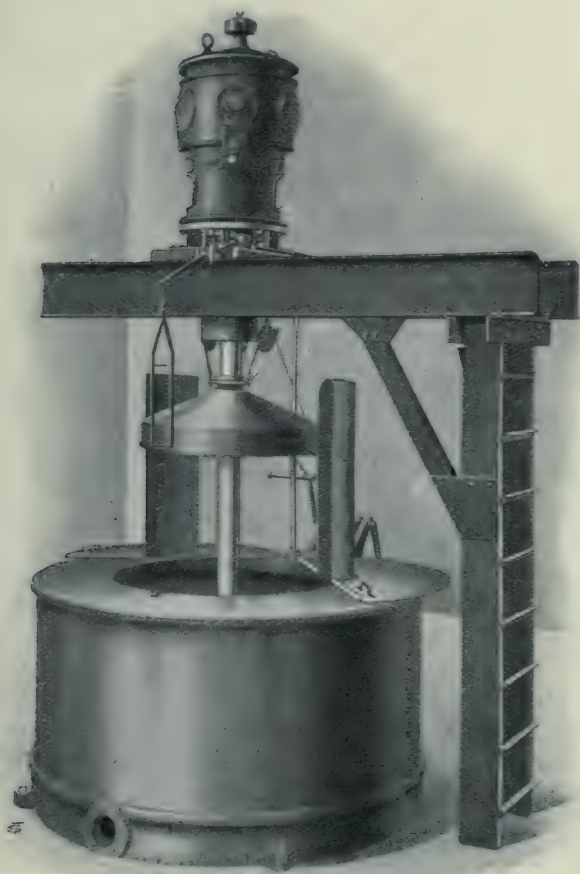
FIG. 17.

to run away perfectly clear, this occurring as soon as the pores in the fabric have become so far obstructed by the projected solids as to allow water alone to pass through. The milky water is then returned to the feed tank and run slowly into the machine. The water is very quickly expelled, and the colour remains in the drum as a stiff paste, of sufficient consistence to be moulded into lumps of any desired shape. The use of the hydro-extractor may be particularly recommended when ample motive power is available and accelerated draining is desirable.

Fig. 17 illustrates a modern type of hydro-extractor with bottom discharge and suspended drum, the shaft of which is coupled directly to an electro-motor.

Filter-presses.—Whereas the hydro-extractor is only used in particular cases for the purpose of the earth-colour manufacturer, the filter-press enjoys more extensive application. Every filter-press is composed of a number of closely fitting press frames, held together by the pressure of a screw. These frames, when assembled, form chambers provided with inlet and outlet openings. Suitably shaped and stitched filter-cloths are secured inside the chambers, and the sludge to be filtered is run into the press from a high-level tank. The water passes through the filter-cloths and runs off, whilst the colour earth gradually fills the chambers. When draining is completed, the press is taken apart and emptied. In this way the earths are obtained in the form of more or less dry cakes, which are then put through further treatment or dried.

Fig. 18 shows a Dehne filter-press suitable for the earth-colour manufacturer. Wood internal fittings are often used, because wood does not affect the shade of the colours; but, wherever the nature of the materials

admits, iron presses are to be preferred on account of their greater durability and the certainty of the joints continuing tight. The finer the grain of the levigated colour, the more difficult the expulsion of the water; but as a rule, a pressure of 115–195 inches, water-gauge, will be sufficient.

If the sludge be run into the press from a tank at sufficient height, two charges can be worked in a day, but the cakes will not be as firm as butter of medium
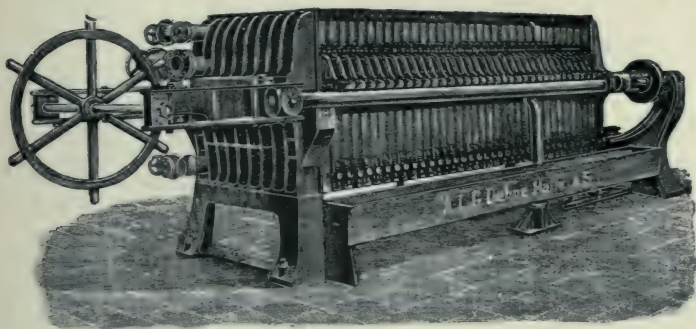

FIG. 18.

hardness. It is better to pump the charge into the press by means of a special diaphragm pump. The drainage is then incomparably quicker, the cakes will be formed in about an hour and will also be drier. A good deal, however, depends, naturally, on the nature of the earth colour.

If the colour contains acid, alkali or salts, the filter-cloths can be washed by flushing the press with water under pressure. The cloths are made of specially fine cotton fabric. The press-runnings, which are never quite clear, are collected in a clarifying tank,

where they are treated with lime and kieserite, whereby gypsum is formed, and the mass is put through a filter-press, which retains the solids and leaves the effluent clear.

Filter-cloths which have become choked by use are spread on a table and scrubbed with water, or else
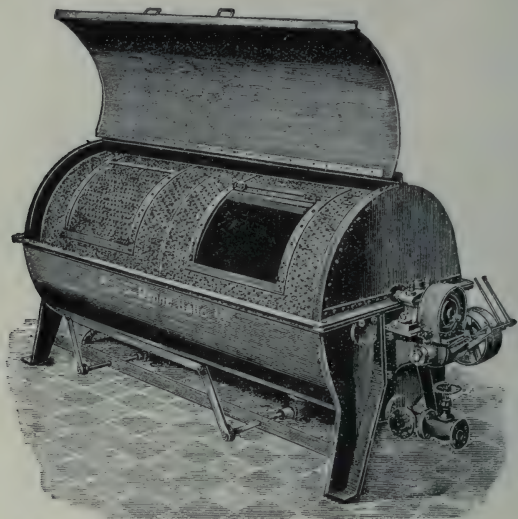

Fig. 19.

washed in a special machine (Fig. 19), consisting of a rotary drum, with belt drive, the rotation circulating the water in the interior trough and enabling it to extract the dirt from the cloths. The flow and discharge of the water are controlled by valves, and the water may be warmed by admitting steam into the machine. The size of the washer depends on that of the filter-cloths.

From the press, the cakes of colour are conveyed

to the drying-plant, usually by the aid of automatic machinery.

Drying Appliances.—The stiff paste or cakes from the hydro-extractor or filter-press can be shaped, but require to be dried before they are put on the market. Drying is a wearisome operation, the finely divided material taking a very long time to dry completely, even during the summer months, whilst in winter it is almost impossible to get certain colours—such as ferric oxide colours and levigated clay—quite dry in the air, the inside of the lumps remaining soft and pasty after lying for months.

The only way in which this troublesome delay in the completion of the operation can be overcome is by artificial drying; but as the employment of artificial heat entails expense, it is necessary to carry on the process with the smallest possible outlay, in view of the low commercial value of most earth colours.

Long experience has convinced the author that the arrangement of the drying-rooms in many colour works is based on entirely wrong principles, and that a great portion of the heat furnished by the fuel is wasted. For this reason the description of a properly arranged drying-room will be welcomed by a number of readers.

It is a well-known fact that hot air is lighter than cold. Consequently, when a room is artificially heated, the highest temperature will be found just under the roof or ceiling, and articles placed in that part of a heated room will dry much faster than those near the floor. If the drying-room is heated by an ordinary stove, articles placed on a fairly low level will only dry very slowly, because the hot air flowing from the stove tends to ascend.

In order, therefore, to utilise the entire space of the

drying-room, it is necessary to place the heating apparatus in such a position that the whole of the room will be warmed as uniformly as possible. The stove should therefore be situated in a chamber underneath the drying-room proper.

Because air that is already saturated with moisture cannot take up any further quantity, care must be taken to remove the damp air continuously from the drying-room, and to replace it by dry air. This may be effected by suitably designed ventilation, on the lines shown in Fig. 20, which represents a drying-room arranged in such a way as to provide for all the above-mentioned contingencies, and ensure continuous drying.

The heating apparatus is located in the cellar, and consists preferably of a slow-combustion stove comprising a cast-iron cylinder, with an air inlet A (with sliding regulator T), for the air of combustion, and a shoot F at the top, through which the stove is fed with fuel—preferably coke, on account of its great heating power.

The stove is surrounded by an iron or brick shell M, having two flues R and $R\iota$ leading to the chambers I and II, where they terminate in register cowls K, which can be adjusted, by turning the handles h, so that when the slots o in K coincide with corresponding slots in the end of the pipe, the maximum amount of hot air from the stove is delivered into the drying-chambers; and, by suitably adjusting the cowls and the draught through the fire-door T, it is possible to regulate the temperature of the chambers to within one degree of the thermometer scale. When only one of the drying-chambers is required to be heated, the register in the other is closed, and the whole of the hot air is delivered to the first one. With this arrangement

none of the heat is wasted, and the contents of one chamber can be dried while those of the other are being removed and replaced.

The moisture-laden air from the drying-chambers can be led direct into the stove chimney. When coke
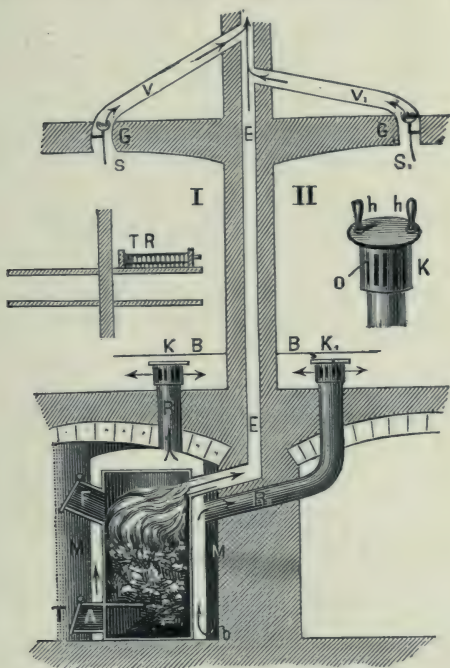

FIG. 20.

is used, the flue gases consist almost entirely of carbon dioxide. If the vent pipes are led from the top of the drying-chambers into the chimney, the hot gases ascending the latter induce a strong draught in the chambers and carry off the moist air into the open. These pipes, also, are fitted with registers, which, when suitably

adjusted, assist in the maintenance of a uniform drying temperature.

The colours to be dried are spread on trays laid on suitable racks in the drying-chambers ; and, by carefully planning out the available space, a very large quantity of colour can be quickly and completely dried in a comparatively small plant. The cost of the fuel is so small as to be more than counterbalanced by the saving of time.

The heating arrangements in drying-rooms are capable of improvement in many respects, especially where steam is at disposal; and in such cases, it is better to substitute steam heating for a fire. It will then be necessary to put in a good fan, or other device, to ensure the removal of the moist air. An excessive room temperature—above, say, 50° C. (122° F.)— is not only superfluous, but in many cases injurious, because, apart from the fact that some colours change in shade when over-warmed, an unduly high tempera-ture causes the surface layers to dry very quickly and form a crust which prevents the escape of water vapour from the interior of the material.

Another form of drying-plant for earth colours is the drying-floor, a large room with a rammed concrete or stone floor, intersected with brick flues (about one foot square), covered with iron or concrete slabs and conveying hot flue gases from a furnace. These floors are particularly suitable where there is a possibility of utilising an existing supply of hot flue gases.

Drying-tunnels are specially adapted where large amounts of material have to be dried. The tunnels are built of brick and provided with a rail track on which the trucks carrying a series of trays laden with colour are run. As the trucks move slowly forward,

they are met by a current of hot air which dries the charge. The tunnel is kept filled with laden trucks, each fresh one introduced pushing a finished one out at the further end.

In many cases, drying troughs are also useful. These are long, semicircular, jacketed troughs of boiler plate, hot air or steam being passed through the jacket space. A worm conveyor keeps the contents moved forward, turned over and mixed to facilitate drying.

Mention may finally be made of vacuum drying-cupboards, which are heated, air-tight chambers, for the material, in which the air is partially exhausted, thus increasing the rate of evaporation of the water and causing the materials to dry quickly at a much lower temperature than otherwise.

Crushing and Sifting

The distributing and covering power of the earth colours depends—apart from their special properties— on the fineness of their particles. For this reason, all the means adopted for the purpose of pulverisation are of particular interest. The most important crushing and powdering devices have already been described, and may be referred to, all that needs mention in addition being the fact that stone mills also are used for fine grinding.

The ground products, however, are not entirely homogeneous, always containing, in addition to the very finest particles, those of a coarser nature which must be removed by sifting.

Sifting machines are essentially sieves through which the colour is passed. The sieves are made of wire gauze or bolting-cloth, stretched on prismatic frames

which are rotated (centrifugal sieves), or superposed on the flat and reciprocated. In centrifugal sieves, the material is projected against the sieve, and the whole apparatus is in a state of vibration, or else beaters are provided to keep the fine orifices in the sieve from choking up.

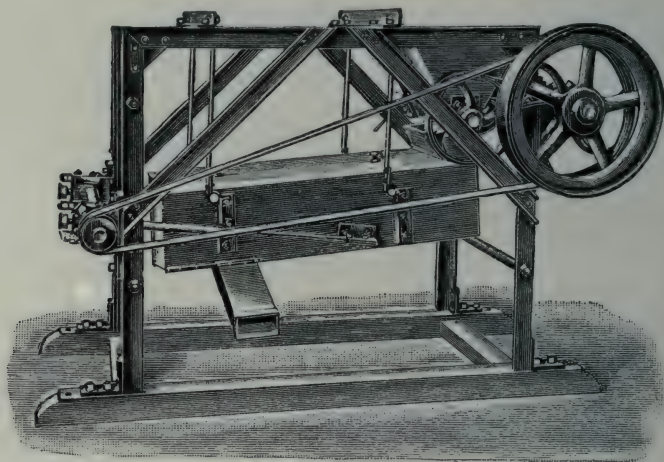Nowadays there are numerous types of sifting

FIG. 21.

devices, none of which, however, can be considered as the best for all purposes, since each type of earth colour behaves differently and requires special treatment. The proportion of moisture in the material, also, has an important influence on the method of treatment required.

A typical flat sifting-machine, with eccentric jig motion, is illustrated in Fig. 21. The machine is fed through a hopper provided with feed rollers, the

rate of feed being adjustable. The screened product is discharged through a shoot at one side of the machine, and the residue at the opposite side, into boxes, etc., placed underneath.

For materials that give off a large amount of dust, the machine can be enclosed in a dust-proof casing, in which event the product and residue are delivered
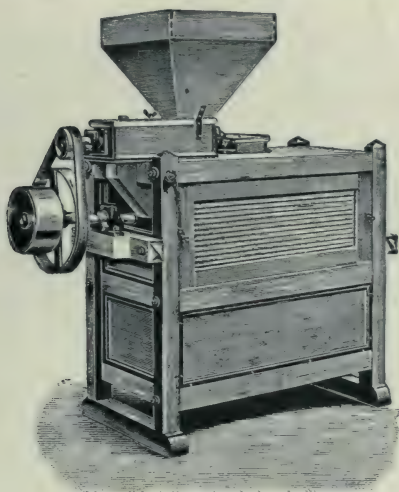

FIG. 22.

into drawers. The machine is easily cleaned and the sieves quickly changed, and is well adapted for dealing with a succession of different materials. The hopper can be fitted with a pair of adjustable crushing rollers.

Fig. 22 is a drum sifter, which is fed by means of a hopper and worm; and the drum can be covered with wire or silk gauze. The sifted product falls into a worm conveyor in the bottom of the casing and is

discharged at the side. This may be replaced by a series of mouths for discharging direct into bags, or the machine can be adapted to deliver into an elevator, worm conveyor or other means of transport to a distance.

The screenings are discharged through a shoot at the back of the machine, and can be handled in various
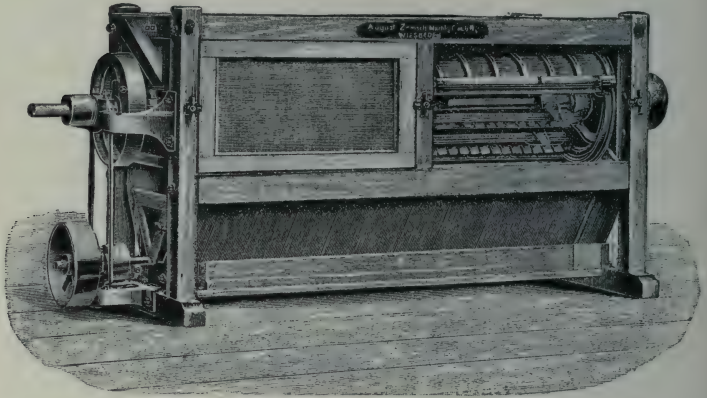

Fig. 23.

ways. A beater is provided to clear the drum and increase the output.

Fig. 23 illustrates a centrifugal sifting-machine for producing very fine powder in large quantities without any escape of dust. It contains a screening drum, the frames of which are detachable and facilitate changing the sieves. A beater revolving inside the drum projects the powder against the sieves, such portions as pass through being taken up and discharged by a worm conveyor; this, however, can be replaced by a bagging device, etc.

Calcining

Colour earths are sometimes calcined at a high temperature in order to modify their structure and shade, the operation being accompanied, in some cases, by the destruction of organic admixtures and the expulsion of volatile constituents.

An important feature of calcining is that it improves the covering power of many colours, especially heavy spar and certain ferric oxide pigments. This alteration is probably due to the heat causing the finest particles to cohere, and also to the expulsion of chemically-combined water, etc.

The change of shade, which is often dependent on the degree and duration of the heating, is probably also connected with cohesion; but in many instances it is attributable to chemical modifications produced by the treatment; ferric hydroxide, for example, losing its water of hydration when heated and becoming transformed into ferric oxide.

The details of the calcination process vary with the nature of the material, and will therefore be described, together with the appliances used, when we deal with the colours which require to be put through this treatment.

Mixing and Improving

It is very important that the maker of earth colours should always be able to turn out his products uniform in shade, and since the raw materials are liable to vary in character, and the composition of the earths from one and the same deposit is not invariable, the desired shade has to be obtained by mixing. For this purpose,

6

standard samples must be prepared, for comparison in matching.

Mixing is a highly important operation, on the proper performance of which oftentimes depends the sale of certain colours and the reputation of the maker. It may be effected in various ways, such as shovelling the ingredients together or by combining the work with grinding in edge-runner mills, ball mills, etc. Another method is the mixing barrel shown in Fig. 24,
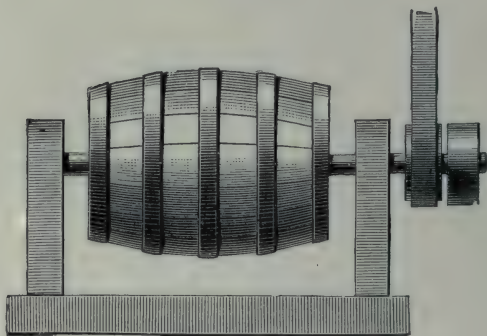

FIG. 24.

a strong cask mounted on an axial shaft driven by a motor, etc. The barrel is filled about two-thirds full of the materials to be mixed, and, after closing the feed door, is slowly rotated, since, if run at excessive speed, the contents are merely projected against the sides of the barrel by centrifugal force, and it can then be turned for hours without result. The mixing effect can be considerably increased by mounting the barrel so that the shaft is offset from the longitudinal axis of the barrel by an angle of about 30°, the contents being then moved from side to side at each revolution

and thus more intimately intermixed by the twofold motion.

In addition to such home-made appliances, there are mixing-machines of the type illustrated in Fig. 25, the body of which is fitted with a distributing worm at the top, and a pair of rollers at the bottom. Below the rollers, which are covered by plates that can be
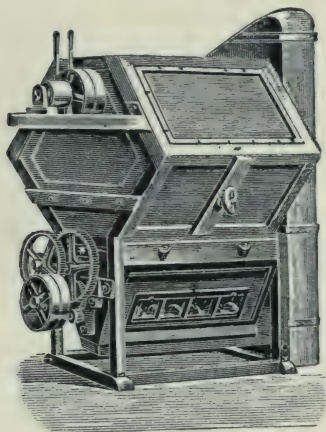
FIG. 25.

adjusted at a convenient angle, is a worm conveyor delivering into an elevator, outside the machine casing, which connects the two worms. One or more discharging-doors, according to the size of the machine, are provided under the worm conveyor at the end next the elevator. The feed hopper can be arranged on the elevator or on top of the machine, according to local conditions.

In working this machine, the elevator and distributing worm are started and the full charge is fed into the

hopper. When it has all passed through the distributor and is lodged on the sloping plates and bottom rollers, the latter and the worm conveyor are set in motion, the material being then carried through by the rotation of the rollers and dropping on to the conveyor, which delivers it to the elevator, to be returned to the distributor. In this way the charge is kept in continuous circulation, and the finely divided particles are repeatedly intermingled, a uniform mixture being obtained. The effect is heightened by the grinding action of the rollers as the material passes between them.

The serial order of the various ingredients, their physical condition (granular or powder), and their density, are all immaterial, the mixing being effected so intimately that when, for example, a colour is shaded with aniline dyes, the ingredients are so completely blended in less than an hour that even the smallest sample then taken will perfectly represent the bulk.

These machines are made in various sizes, are entirely automatic, both in charging, discharging and mixing, and are quite dust-proof, the consumption of power being also small. If necessary, they can be combined with a crusher or sifter feeding direct into the hopper.

A simple means of ascertaining whether the mixing is completed, and one that can also be employed for judging the character of ground materials, consists in placing a sample of the product on a sheet of white paper and spreading it out, under gentle pressure, with a steel or horn spatula. No irregularities, streaks, spots or granules should then be discernible either by the unaided eye or under a magnifier.

Improving, which consists in staining earth colours with other (usually organic) colouring agents, to improve the shade, is an operation which is generally resorted

to only in case of need, because it means extra expense, and is of no value unless light-proof colours are used. No permanent effect can be obtained by merely mixing-in coal-tar dyes at random. In addition to certain organic dyestuffs, artificially prepared mineral colours and colour lakes—artificial preparations of an organic dyestuff with an inorganic substratum—are also used for improving.

Another way of improving earth colours is by precipitating certain coal-tar dyes on them, in presence of a fixing agent. Of course the dyes used must not only be fast to light, but also inert towards the substratum and to any other ingredient, such as lime, that is subsequently added to the earth colours.

The following dyestuffs (Höchst) are suitable for direct precipitation on siliceous colours (green earths, clay, ochres, etc.).

Auramine, conc. O, I, II; new phosphine extra; chrysoidine A cryst., B cryst., C extra; Vesuvine (all marks); cachou brown D, G; dark brown M, MB; safranine G, GS conc., B conc.; rhodamine O extra, B, B extra; fuchsine (all marks); fuchsine acetate; cerise G, R; grenadine O, R, RR; maroon O extra; new fuchsine O, P; methylene violet (all marks); peacock blue P; Victoria blue B, R; thionine blue GO; methylene blue (all marks); malachite green (all marks); brilliant green (all marks); coal black O, I, II.

MOULDING

The colour pulp can be made into tablets by moulding it in dry boxes divided into a number of compartments. The colour shrinks in drying, and the tablets will then easily fall out of the moulds. Cones are obtained by

placing the pulp in a box, the bottom of which is perforated with numerous holes of uniform size, the box being then tapped against the surface of a stone table. At each stroke, a certain amount of colour is forced, in the shape of small cones, through the perforations, on to a sheet of paper underneath. The cones are then dried.

Some colours are moulded into blocks by forcing the partly dried paste into suitable moulds—preferably of metal, so that they may be engraved with the maker's name, or other imprint—and left to dry slowly and without cracking. The cakes may be prevented from crumbling by incorporating a small quantity of adhesive, such as a weak solution of dextrin, with the water in which the colour is suspended.

CHAPTER IV

WHITE EARTH COLOURS

THE white earth colours are important for the purposes of the colour-maker, because not only are they used by themselves as paints, but also serve in the production of light shades of other colours.

The white colours containing clay or lime are the most abundant and important of all, and will therefore be described first. The lime colours comprise caustic lime, carbonate of lime (chalk or powdered limestone), gypsum and bone ash.

CAUSTIC LIME

Though this product is not used direct as a painters' colour, it is employed in the preparation of compounds that are so used. It is made on a large scale for the preparation of mortar, and there is therefore no need for the colour-maker to manufacture it himself, since it can always be bought from a lime-burner. It must be borne in mind, however, that lime for the colour-maker's purposes must possess certain properties, failing which it is of no use to him. What these properties are and how the product is made will now be briefly described.

When carbonate of lime, *i. e.* native limestone, is

exposed to strong heat it parts with carbon dioxide and is transformed into burnt or caustic lime.

$$CaCO_3 \quad = \quad CaO \quad + \quad CO_2$$

Carbonate	Caustic	Carbon
of lime.	lime.	dioxide.
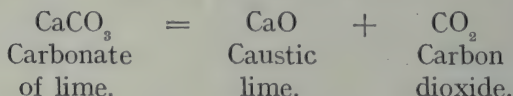
The limestone is burned either in kilns of very simple construction, or else in more complicated furnaces in which a continuous process is maintained. The ordinary limekiln, which can be found in many parts of the country, consists merely of four walls, with a door in the front one for the introduction of the fuel. Kilns of this kind are usually set up in the vicinity of the limestone deposits, and are abandoned when they get worn out.

The limestone is broken to lumps of fairly even size, about as large as a man's head, and these are piled up in a domed heap in the kiln, sufficient space being left between the lumps for the passage of the flame. A fire is then lighted under the pile, pine wood being mostly used for this purpose on account of its high content of resin, which gives a very strong flame. The fire is kept up until the top of the pile has become white hot, and only a blue, smokeless flame is visible. The appearance of this denotes that the burning is ended, the fire being then allowed to die out and the lumps left until cool enough to be taken out of the kiln.

This operation is performed with great care, particular importance being attached to preserving the lumps as intact as possible and preventing the formation of dust, which is of little value. The lime made in this way is endowed with properties that render it valuable for the purposes of the colour-manufacturer; but, on the other hand, possesses certain disadvantages.

Owing to the use of wood as fuel, the caustic lime obtained in this way is usually a very pure white, because the burning is continued until the whole mass is glowing and the firewood has been completely consumed. If this is not the case, the burnt lime is greyish in colour, from the finely divided particles of carbon, which, of course, spoils the lime for colour-making. The defects existing in lime burned in the above type of kiln originate in the irregular character of the product. It will be evident that the limestone lumps that are nearest the fire will be far more strongly heated than those in the upper part of the dome; and when calcined lime is kept incandescent for a long time, it becomes so compact in texture that it quenches with great difficulty when brought in contact with water. This condition is known as "dead burnt," and such lime is of little value.

The lumps at the top of the pile are least exposed to the heat, and very often still contain carbonate, as is shown by the effervescence produced on treatment with an acid. Such lime is imperfectly burnt, and the lumps frequently still exhibit the crystalline structure of limestone when broken. They quench rapidly, but when mixed with a little extra water, the mass is no longer of the buttery consistency typical of caustic lime, but contains gritty portions consisting of unaltered limestone.

Owing to the defects of dead burning on the one hand and insufficient calcining on the other, colour-makers now prefer lime that has been burned in continuous kilns, because, when properly made, such lime is very uniform in character, and is also cheaper than that burned with such an expensive fuel as wood. In consequence of the greater capacity of the continuous

kiln, and the more uniform character of the product, the old-fashioned kilns are more and more falling into disuse.

The arrangement of the continuous kiln is very simple. The kiln consists of a fairly high shaft, open at the top, and provided at the bottom with a small hole for the removal of the burnt lime. A coal fire is lighted, and as soon as the kiln is heated up, alternate layers of limestone and sufficient coal for burning it are introduced. The burnt lime sinks to the bottom of the shaft and is pulled out, with iron hooks, from time to time.

Given the right proportions of coal and limestone, the lime made in these kilns is burnt to just the right degree, and is excellent for builders' use. In many cases, however, it is less valuable to the colour-maker, and in some quite useless. For example, when the coal is not completely consumed, carbon, even though only a very small quantity, is deposited on the lime, and the burnt lime, instead of being a brilliant white, as it should be, is grey ; and colour made therefrom is also greyish white and will spoil the shade of other colours with which it is mixed.

The chemical composition of the original limestone also has an influence on the character of the burnt lime. Limestone consisting entirely of carbon dioxide and lime is so rare that sufficient is never available for making burnt lime on a large scale. Even the purest limestone found native in large quantities— namely marble—is not pure carbonate of lime, but contains a certain proportion of extraneous substances. At the same time it is too expensive to use for technical purposes.

The ordinary impurities present in limestone are

ferrous oxide, ferric oxide, magnesia and organic matter. The presence of ferrous oxide can usually be detected by the greenish tinge of the raw limestone, and the reddish cast of the burnt product. Ferric oxide is revealed by its reddish colour, in both the limestone and burnt lime.

Magnesia, which is present, for example, in dolomitic limestone, cannot be detected by the colour, either before or after burning, this oxide being itself perfectly white; but its presence is a drawback because if in large quantity it makes the lime very difficult to quench, and such lime is never of a fatty character.

Organic matter betrays itself by the colour, the lime being dark tinted, varying from grey to black. Black limestones usually contain carbon in an extremely fine state of division, and are quite useless to the colour-maker owing to the impossibility of completely burning off this contained carbon, which always imparts a greyish tinge to the burnt lime. The behaviour of limestones in this respect varies, however, considerably, and can only be ascertained with certainty by a trial burning. Many that are rather dark in colour will, nevertheless, burn perfectly white, whereas others, much lighter in shade, always give a product that is not quite pure in tone. This divergent behaviour seems to have some connection with the chemical composition of the organic matter in question. If it consists of coal, or substances analogous thereto, no really pure white lime can be obtained from a light grey limestone, it being impossible to burn off the finely divided carbon completely.

In addition to making a trial burning with a fairly large sample of material, the behaviour of a limestone towards hydrochloric acid will afford some information

as to the nature of the grey colouring matter. If the
limestone dissolves completely when suffused with the
acid, the indications are favourable for its usefulness
to the colour-maker. If, on the contrary, a black
residue is left, the coloration is due to finely divided
carbon, and there is then little prospect of the material
furnishing a suitable product. In any event, a trial
burning is the most reliable guide. In addition to
carbon, the presence of any large proportion of ferric
or ferrous oxide is objectionable, since, in either case,
the product will be tinged red with ferric oxide, into
which the ferrous oxide is transformed at calcination
temperature.

In addition to comparing the colour of the product
with a standard sample, the suitability of a burnt lime
for colour-making can be tested by quenching. If a
lump about the size of the fist be placed in a large
porcelain basin and suffused with a small quantity of
water, preferably poured in a thin stream, the lime,
if properly burned, will continue to absorb the water
for a considerable time, like a sponge, and will very
soon give evidence of a brisk reaction by increasing
in bulk and generating such an amount of heat as to
cause the immediate evaporation of a few drops of
water allowed to fall on the surface of the mass.
Finally, the entire lump will crumble down to a very
delicate, voluminous powder, consisting of slaked lime
(calcium hydroxide).

This chemical reaction is expressed by the
equation :—

$$CaO \quad + \quad H_2O \quad = \quad Ca(OH)_2$$
Lime   Water   Calcium hydroxide.
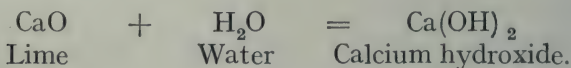
When the amount of water added to burnt lime is

no more than sufficient to effect its transformation into
hydroxide, this latter, as already stated, forms a deli-
cate white powder. The addition of more water results
in the formation of a homogeneous pulp, of a peculiar
fatty character. Since this fatty appearance is only
possessed by pure lime, it is a criterion of high quality
in burnt lime, and contrasts strongly with that of the
less valued poor (or lean) lime.

Calcium hydroxide acts as an extremely powerful
base, and therefore must not be mixed with colours
that are sensitive to the action of strong bases. As a
matter of fact, its direct use in painting is very small.
Of course, a thin milk of lime is used for whitewashing
walls, etc. ; and if any colouring ingredients are added
they must be such—e. g. ochres—as are not affected
by the lime. Nevertheless, quick and slaked lime are
very important in colour-making, as forming the
originating material for the preparation of a number
of colours.

When slaked lime is mixed with sufficient water to
form a stiff pulp, and is left exposed to the air for some
time, a change will be observed to take place, the mass
solidifying gradually (commencing on the outside) and
finally crumbling to a soft white powder. This change
is due to chemical action, the lime having a great
affinity for carbon dioxide, which it readily takes up
from the atmosphere—a fact which explains the
solidification mentioned. It would be erroneous to
assume that the lime is again completely converted
into calcium carbonate in this way; for, though such
conversion does ultimately take place, it requires a
very long time for completion.

The resulting compound is, actually, a double com-
pound of calcium oxide and carbonate. Although this

compound has fairly strong basic properties, they are, nevertheless, far weaker than those of caustic lime, being partly neutralised by the carbon dioxide absorbed. If the superficial area of the slaked lime be increased by spreading it out thinly, so as to offer greater opportunity for the action of carbon dioxide, the formation of the double compound in question will be greatly accelerated.

This double compound is prepared artificially in special works, and the resulting colours are put on the market under various names. They, too, must not be mixed with colours that are sensitive to alkali, and on this account they cannot be used in fine paints. If applied as a white priming to the walls of rooms, care must be taken to cover the coating with some substance that will protect the topping colour from the action of the lime. For this purpose, painters use a wash of milk, soap and water, etc.

An important property of lime is its behaviour towards casein, the substance forming the curd of milk. With this body it combines to form a mass which sets hard and is highly resistant, viz. calcium caseate, and is formed when limewash is stirred up with milk or freshly precipitated casein. Weatherproof distempers for outside use are prepared in this manner.

PEARL WHITE

The preparation frequently met with in commerce under this name is nothing more than a burnt lime of great purity. It is prepared in the coastal districts by burning oyster shells, the resulting burnt lime being easily transformed into a fine powder, the pure white colour of which is due to the absence of iron. It is used in the same way as pure burnt lime, and is mainly

of interest in seaside towns where oyster shells are often accumulated. It may be pointed out that the name pearl white is often applied also to pure white grades of white lead.

Vienna White

This colour is prepared from any kind of burnt lime that is sufficiently pure ; that is, free from ferric oxide. The method of preparation is simple, requiring no special apparatus, and can therefore be carried out wherever suitable lime is available.

Operations are commenced by carefully slaking well-burnt lime with water, a sufficient excess of which is added to produce a fairly thick pulp. To accelerate the absorption of carbon dioxide, the mass is exposed to the air in thin layers, by spreading it out on boards, so as to present a large surface to the air. As soon as the pulpy character has disappeared, the mass is detached from the boards, and is pressed and kneaded, with wooden paddles, into prismatic cakes which are left exposed to the air—being, of course, protected from the wet—until the absorption of carbon dioxide is complete—a condition that can be recognised by the earthy character of the product. The cakes are then dried, an operation entailing great care, since lightness is a sign of good quality, whereas a damp product is very heavy.

In forming the cakes they must not be touched by the bare hands, because the lime is so caustic that it would soon destroy the skin. The foregoing method of manufacture is capable of many improvements, which can be introduced without adding much to the cost of production.

If the lime is formed into large blocks, it will evidently

take a long time for the mass to acquire, all through, the earthy character indicating combination with carbon dioxide. This drawback can be easily remedied by forming the mass into small cakes, which will become ripe, owing to their larger surface, much sooner than the bigger blocks.

A very good plan to adopt in moulding is to form the burnt lime into a stiff paste with water, preferably by adding enough water to make a viscous mass, and leaving this in a lime-pit for several weeks, the prolonged storage enabling the lime to acquire the already mentioned fatty character, and at the same time to become highly plastic. Lime treated in this way can be forced through a nozzle, forming a cylindrical rope, which can be cut by a knife into convenient lengths and left on boards for a few days until they have become firm enough to stand up without breaking. Cylinders made in this manner, with a length of about four inches and a diameter of two inches, will absorb carbon dioxide very quickly.

The absorption can be still further accelerated by setting up the cylinders in an atmosphere highly charged with the gas, for instance in the vicinity of a manure pit, as they will then avidly take up the carbon dioxide abundantly liberated from the rotting manure. Similar acceleration will take place if the boards carrying the cylinders are placed in a stable, or in a room where wash for making spirits is fermenting, because large quantities of carbon dioxide are liberated in both places.

Working the caustic mass by hand is accompanied by so many inconveniences that it seems highly desirable to employ some mechanical moulding device which will render contact with the wet lime entirely

superfluous. It may be pointed out that such a device can also be advantageously used for moulding all earth colours in paste or pulp form, and in particular for shaping ferric oxide colours into rods or small cylinders.

Such a machine (Fig. 26) is composed of a rectangular box with semi-cylindrical bottom, a detachable shaft carrying a sheet-metal worm being arranged in the box so that the worm is in contact with the rounded bottom and is continued into the cylindrical extension of the
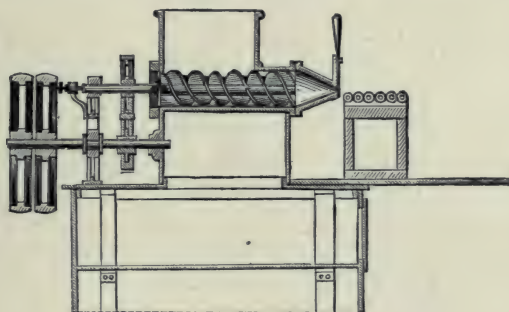

FIG. 26.

box. This extension terminates in a hollow cone, to the mouth of which nozzles of varying aperture (square, rectangular or round) can be attached. A knife, operated by hand or mechanical means, enables the extruded soft mass to be cut into convenient lengths, which drop on to a series of easy running rollers in front of the nozzle, and are thereby delivered to an endless-belt conveyor from which they can be transferred to the drying-boards.

When the box has been charged with the lime pulp and the worm is rotated, the latter forces the soft mass into the cone and extrudes it through the nozzle, so

that, as long as there is any material in the box, it is discharged as a continuous rope, of square, rectangular or cylindrical section, on to the guide-rollers, where it can be cut off into lengths by the knife.

A fundamental condition for the preparation of a good Vienna white is the employment of pure raw material, which must be free from ferric oxide or earthy impurities, and fully burned. An excellent material for this purpose is calcined mussel shells, which furnish a loose, and at the same time very pure, lime, and are very largely used for lime-burning in places such as Holland, where they are available in large quantities.

Vienna white is not much used as a paint colour, owing to its powerful alkaline properties which have a destructive effect on many colours. It is, however, largely employed as a polishing agent, for which purpose it is powdered and is put on the market—mostly in bottles—as Vienna lime. Its very handsome white colour and low price render it particularly suitable for coarse painting, for example as a prime coating for painted interior walls. To guard against the danger of the painted decoration being destroyed by the alkaline nature of the white, it is advisable to coat the dried ground with alum solution, the alumina of which combines with the lime to form an insoluble compound to which organic colours adhere well. The sulphuric acid also enters into combination with the lime, the resulting gypsum having no effect on the paints subsequently applied.

Chalk

The name chalk is used for a number of commercial substances which differ considerably in both the

mineralogical and chemical sense. French chalk, for instance, is a mineral belonging to the steatite group and, apart from its name, has nothing in common with true chalk, except the white colour, and even this differs altogether from that of chalk properly so called. It is therefore necessary, in the interests of proper nomenclature, to differentiate the various kinds of chalk, commencing with the mineral known by that name to the chemist and mineralogist.

In chemical composition, true chalk is calcium carbonate, but of a fossil character, for if chalk dust be examined under a high-power microscope, it will be seen to consist of the shells of minute animals, and is therefore to be regarded as fossil. The organic matter of the animals has long disappeared, leaving the inorganic material, a very pure calcium carbonate, behind.

Such progress has been made that the zoological status of the animals which inhabited the shells—many thousands of which are present in a lump of chalk—has been identified; and it is known that these animals were of marine type. Fig. 27 shows the appearance of the animal remains in Meudon chalk when highly magnified, the upper half being viewed by transmitted light and the lower by reflected light.

Notwithstanding the extremely minute dimensions of the chalk animalculæ, their remains form rocks of great thickness in all parts of the world. In Europe we find, for example, extensive chalk formations in England, whose Latin name Albion was bestowed on account of the white chalk cliffs occupying long stretches of the coast. The hills of Champagne consist almost entirely of chalk; and Rügen, together with many other islands, is nearly all chalk cliffs.

It is only in very rare cases, however, that chalk occurs in sufficient purity to be immediately suitable for use as a pigment or writing-material. For the most part it contains other minerals, or large fossils, from which it has to be separated by mechanical treatment. Nodular flints are often met with in chalk, and many deposits contain such large numbers of the petrified shells of the sea urchin that the chalk really cannot be used as a pigment at all, by reason of the high cost
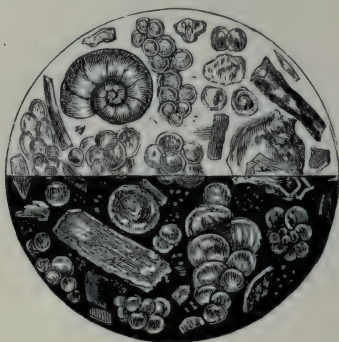

FIG. 27.

of purification. The only places where chalk can be advantageously worked for the preparation of pigment is where the mineral is in a high state of purity, and also contains only very few sandy particles. Such chalk deposits are worked on a mining scale, and, as a rule, in the state in which the chalk comes from the quarry; it is in the form of a soft mass, easily scratched with the finger-nail and of fairly high density, owing to the considerable quantity of water with which it is ordinarily impregnated.

In order to convert this crude chalk into a product that can be used as a pigment, it is first left to dry

until the lumps can be easily broken, and then crushed into small pieces, from which all the extraneous minerals, which occur as large lumps, are sorted out and removed. This picking process is important, especially when the chalk contains flints, because these latter are very hard and would injure the millstones in the subsequent grinding.

The lumps of chalk are reduced by mechanical means, such as a stamp-mill, or, more frequently, in a mill of the same type as for grinding flour, since it is impossible to get the lumps so dry as to produce the degree of brittleness necessary for a thorough reduction in a stamp-mill. The millstones are enclosed in a wooden casing, and the chalk is ground in admixture with water, the ground mass escaping, through an opening in the casing, as a thick pulp which is stored for a considerable time in large tanks.

Experience has shown that this method of prolonged storage in contact with water greatly improves the colour. The only explanation of this fact is that the chalk still contains a very small amount of organic matter, which gradually decomposes in presence of water. The evidence in favour of this is the peculiar smell given off during storage.

Even with the most careful grinding, chalk cannot be transformed into such a fine powder that is directly fit for all purposes; and the only way to obtain the requisite fineness is by levigation. Owing to the large quantities that are usually handled in this process, the milky liquid coming from the mill is mostly run into large brick tanks, where it is left to settle until all the chalk has deposited and the supernatant water is perfectly clear. Tapping-off being usually impracticable, the water is generally drawn off by careful

syphoning, so as not to disturb the fine sludge at the bottom of the tank.

The deposit in the settling-tanks is shovelled into wooden boxes, perforated at the sides to enable the water to drain away, the chalk being prevented from escaping by lining the boxes with linen cloths. The pulp soon loses its liquid character and shrinks considerably, the boxes being then filled up with more sludge, and so on until the contents have ceased to shrink. When the mass is so far dry that it will no longer run when lifted, the boxes are covered with boards and inverted, discharging the contents on to the boards, on which the mass is left to become quite dry. Filter-presses are also used.

Large prismatic masses of chalk never dry so uniformly as to prevent the formation of cracks, and if the chalk is to be sold in this form the cracks are plastered up with thick pulp; this operation, however, being superfluous when the chalk is to be sold as powder.

In order to obtain a more compact product and accelerate the drying of the moulded lumps, some makers use presses, in which the fairly dry chalk is subjected to progressive heavy pressure.

Owing to the fineness of the component particles of chalk, they adhere so firmly together, without any bind, that a fair amount of force is necessary to break down a piece of perfectly dry levigated chalk. Sometimes, however, chalk exhibits the unpleasant property of losing its cohesion almost completely when dry, and in such cases it can only be shaped into prisms with great trouble. This peculiarity is specially accentuated when the chalk contains magnesia; and in order to mould chalk of this kind into blocks, a binding agent,

such as ordinary glue, must be added to the water used in grinding, care being taken not to use too much, or the chalk will become too hard, when dry, for certain purposes, e. g. as drawing or writing chalk.

For some purposes, chalk is sold in powder form, and very high purity is not then essential, an admixture of magnesia or clay being harmless. Gilders, for instance, use large quantities of chalk for priming picture frames, and stir the chalk up with a certain amount of bind (mostly size), to give the particles the desired cohesion.

The chief requirement exacted of a good quality chalk is a handsome white colour; and this depends entirely on the quality of the raw material, not on the method of preparation. It is known that a substance quite devoid of colour will furnish a perfectly white powder, because the colourless particles reflect the light in all directions without breaking it up into its constituent yellow, red and blue rays. Chalk, too, is in reality a colourless substance, and reflects light with greater uniformity in proportion as the fineness of the particles increases. Consequently, when one has a chalk that is not perfectly white, it can, nevertheless, be made to furnish a very handsome product by bestowing great care on grinding and levigation. Properly prepared chalk should be as fine as the finest flour.

When the colour of the best grades of chalk are compared with what may be termed pure white—such as that of white lead, zinc white, permanent white— a skilled eye will always detect a greyish or yellowish tinge in the former, even if obtained from the whitest Carrara marble.

The grey tinge is due to the presence of organic

matter, which cannot be eliminated by any known means, but which can be shown to exist by the fact that when such chalk is heated to incandescence in the air for a short time, the resulting burnt lime is pure white, the organic matter having been burned off. A yellow tinge is caused by minute traces of ferric oxide, which—as also ferrous oxide—almost invariably accompanies calcium carbonate; and limestone free from determinable quantities of these oxides is of rare occurrence. Ferrous oxide does not reveal its presence in limestone unless in large proportion, its pale green colour being of low tinctorial power, whereas ferric oxide, which is a very strong colouring agent, can be more readily detected.

To those who are engaged in the manufacture of white earth colours, however, it is quite immaterial whether a limestone or chalk contains ferrous oxide, because that oxide quickly changes into ferric oxide in the finely divided product, and a chalk which was originally pure white will become decidedly yellow in a short time.

Fortunately, such a yellow-tinged product can be rendered perfectly white by simple means and at small cost, all that is necessary being to add a suitable quantity of a blue colouring matter. When this has been done, the chalk will seem pure white to even the most skilled eye.

This result of adding a blue pigment is based on the well-known physical fact that certain kinds of coloured light produce white light when combined, the colours that give this effect being termed "complementary." A pure blue is complementary to a yellow with a reddish cast—*e. g.* ferric oxide—and therefore a chalk that is tinged yellow by a small quantity of ferric oxide can

be changed into a seemingly pure white substance by the addition of a blue pigment.

The only pigments of use in this connection to the colour-maker are such as have very intensive colouring power and at the same time are low enough in price. Such substances are ultramarine, smalt and coal-tar dyes. Smalt is the best because its colour is unalterable. In point of chemical composition, this substance is a very hard glass coloured blue by cobaltous oxide. For improving the colour of chalk or any other white, the smalt must be in an extreme state of fine division, and levigated to an impalpable powder. Ultramarine can be used for the same purpose, but is not so permanent.

To ascertain the correct proportion of blue pigment, it is advisable to make a systematic experiment, which is easily performed. Exactly 90 parts of the chalk in question are triturated with 10 parts of blue pigment in a mortar until the entire mass has become a perfectly uniform pale blue powder, which contains 10% of the blue ingredient.

Several samples, each representing one hundred parts of the white pigment to be corrected are carefully weighed out, 1 part of the blue powder being added to the first sample, 2 parts to the second, 3 to the third, and so on, and the mixtures are compared with a standard white substance, such as best white lead or zinc white, to see which most nearly approaches the standard colour. It is then easy to calculate how much of the blue requires to be added to 100 or 1000 lb. of the material to be corrected.

The correction can be effected in several ways; for instance, by grinding the blue pigment directly with the bulk, by adding it at the levigation stage, or mixing

it with the dry, finished product. The first two methods are attended with certain drawbacks which render it difficult to obtain a perfectly uniform product, owing to the specific gravity of the blue pigments being higher than that of the whites. Consequently, when the two are mixed in presence of water—as is always the case in grinding and levigation—the heavier blue pigment settles down more quickly, and several strata can be clearly distinguished in the sediment. The upper layers will still have a decided yellow tinge—the proportion of blue being too small for proper correction—whilst the next in order will be pure white—accurately corrected—and those at the very bottom will be decidedly blue, because they contain the largest proportion of the blue substance.

The most satisfactory results are obtained by dry mixing; and this can be successfully practised when the colour-maker has a cheap source of power (such as water power) available. Where, however, costly power plant has to be provided, only the finest grades of white pigments can be improved in this way, the expense of labour being too high for cheap materials.

As a pigment, chalk possesses many valuable properties. The organic structure of chalk gives it high covering power as a wash, a thin layer applied to a surface sufficing to mask the colour of the underlying ground completely. The lime in chalk being combined with carbonic acid, its basic properties are so extensively weakened that chalk can be mixed with even the most delicate colours without fear of their shade being affected. A coating of pure chalk paint on any surface will never change colour in the air; and on this account, chalk is extensively used both as an indoor wash and by wall-paper manufacturers.

PRECIPITATED CHALK

Many chemical processes furnish soluble salts of lime that constitute a by-product of little value. These salts, however, can be advantageously utilised for the preparation of an artificial chalk which is preferable to the native article in many respects. For instance, where large quantities of calcium chloride solution are available, and soda can be purchased at a sufficiently cheap rate, they can be converted into artificial chalk, because these two substances react on each other, forming, on the one hand, calcium carbonate, which is precipitated as a very delicate, insoluble powder, and on the other, sodium chloride, or common salt, which remains in solution, according to the equation :—

$$CaCl_2 + Na_2CO_3 = CaCO_3 + NaCl.$$

If, however, these solutions were mixed together in a crude state, the resulting product would be of only low value as a pigment, being of a yellow tinge and never pure white. This is due to the fact that the impure lime salts, being waste products from chemical works, frequently contain fairly large amounts of ferric oxide, and the soda also is often so high in that impurity that the colour of the precipitated chalk is considerably impaired.

Fortunately, there is no difficulty in eliminating this ferric oxide by chemical means, and obtaining a product of superior colour to the best native chalk. This is effected by treating the perfectly neutral lime-salt solution with calcium carbonate, which causes the precipitation of the iron, a corresponding amount of lime passing into solution.

In order to eliminate the ferric oxide from the lime-

salt solution so completely that not even the most delicate chemical test known will be able to reveal any trace remaining, the solution is placed in a vat and stirred up with finely powdered chalk. If the solution contains any free acid, effervescence, due to the liberation of carbon dioxide, will take place ; and in such event the addition of chalk is continued until the free acid is all neutralised, and the added chalk sinks to the bottom undissolved. The chalk should be in slight excess, so that a decided sediment is visible at the bottom of the liquid when at rest.

This deposit is stirred up again at intervals with the liquid for several days. When ferric oxide is present, the colour of the deposit will gradually change to a yellowish brown, through the precipitation of ferric hydroxide by the chalk; and in this way the final traces of iron can be removed.

The liquid is then carefully drawn off, without disturbing the sediment, and the soda solution is run in so long as a precipitate of calcium carbonate continues to form. The completion of the reaction can be ascertained by pouring a small quantity of the liquid into a tall, narrow glass, leaving it to clarify, adding a little more soda solution and observing whether any further precipitate is produced. On the other hand, it may be that an excess of soda has already been added in the precipitating tank ; and this can be determined by testing a sample with turmeric paper—blotting-paper soaked in a solution of the colouring-matter of turmeric root—which is turned brown by alkaline reagents. Even in very dilute solution, soda will give this colour change, and the test is therefore very accurate. The complete precipitation of the lime in the solution can be ascertained by passing a small

quantity through blotting-paper and treating it with a little acid potassium oxalate solution, which, if lime be present, will at once produce a strong crystalline precipitate of calcium oxalate, which is only very sparingly soluble in water. If the oxalate gives merely a slight turbidity, the residual amount of lime is so small that the process may be regarded as complete.

Since carbonate of soda is usually much dearer than the lime-salt liquor, it is preferable to leave a small quantity of the lime unprecipitated. Given sufficient care in effecting the precipitation, and especially when fairly strong solutions are used, a brilliant white precipitate of calcium carbonate is obtained, which is in such a finely divided state that the minute constituent crystals can only be detected under a high magnifying power.

This precipitated chalk being already in an extremely fine condition needs no further preparation, and, when washed, is ready for immediate use, forming a handsome pigment with excellent covering power.

When precipitation is ended, the deposit is allowed to settle down, and the clear supernatant liquid is carefully drawn off so as not to disturb the delicate sediment, which is then stirred up thoroughly with clean water, left to subside, washed again, and then spread out to dry on cloths which are suspended by the four sides. The surplus water drains away and the residue gradually assumes the consistency of paste, in which condition it can easily be moulded to any desired shape. If left long enough to dry completely, it forms a very delicate powder, furnishing a pigment of excellent quality.

If this precipitated chalk be moulded into prisms for sale, the blocks are laid on one of their broad sides

until firm enough to turn over on to one of the narrow
faces, slabs of gypsum being used as the supporting
material, in order to ensure uniform drying. The
gypsum absorbs water with avidity and thus dries the
prisms evenly.

A defect of these prisms is their great fragility; but
their strength may be improved by mixing a little
very weak solution of dextrin to the mass after the
last washing-water has been completely removed. In
drying, the dextrin binds the material of the prisms
sufficiently to keep them from breaking except under
the influence of a fair degree of force.

Calcareous Marl

As already mentioned, calcium carbonate rarely occurs
in a perfectly pure condition in Nature; and chalk,
also, is frequently contaminated by other minerals.
A variety of limestone occurring as extensive deposits
in many places is that in which calcium carbonate
is associated with clay. Sometimes the clay pre-
dominates, and the mineral is then known as marl,
being really a clay contaminated with chalk. If,
on the other hand, the chalk forms the chief constituent,
the mineral is termed calcareous marl.

Calcareous marls are used in much the same way as
limestone, some modification, however, being necessi-
tated by the presence of the clay. Although limestone
containing a certain amount of clay can be burned in
the kiln, it yields an inferior lime that is of little use to
the builder owing to its low binding power. Marl
of a certain composition finds an important application
in the manufacture of hydraulic lime or cement.

The only kind of marl suitable for pigment is that

containing clay with very little colour; and this is of somewhat rare occurrence, because most marls contain sufficient ferric oxide to give them a yellow shade. Marl that is fairly free from ferric oxide, however, can very well be used as pigment; and many white pigments sold as " chalk " are really finely ground marl.

In accordance with the general practice, in the colour industry, of giving colours a great variety of names, and suppressing the real names, which, so far as the artificially prepared colours are concerned, should bear some reference to their chemical composition, numerous white earth colours bear fancy names, though really consisting of chalk, lime (generally marl), or white clay.

In France, where both chalk and clay are of frequent occurrence—the soil of Champagne, for instance, being all chalky—the manufacture of the white earth colours is extensively practised, and a large number are put on the market, usually named after the place of origin, and consisting of either calcium carbonate or marl.

The trade names of the white earth colours include Cologne chalk, Bologna chalk, Briançon chalk, Champagne chalk, Blanc de Bougival, Blanc de Meudon, Spanish white, Blanc d'Orleans, Blanc de Troyes, etc. All are either more or less pure chalk, marl, or a fairly white clay, pipeclay—which is also used for making clay pipes and for removing grease spots.

GYPSUM

The mineral known as gypsum, or alabaster, consists of calcium sulphate, or sulphate of lime, its composition being expressed by $CaSO_4 + 2H_2O$. In gypsum the

crystalline structure is just discernible, whilst other varieties, such as the so-called " marine glass," occur in considerable quantities as large, perfectly transparent masses. " Russian glass " consists of large, transparent lumps possessing the specific property of gypsum, viz. that of cleaving in two directions, in a high degree. Alabaster is composed of finely granular masses, which are either quite white, or else yellowish, or traversed by grey veins. This variety of gypsum is very abundant in central Italy, and the best blocks are employed for the production of works of art.

Ordinary gypsum, which frequently occurs in the vicinity of dolomitic limestones, is found in a great variety of colours, bluish-grey, yellowish or reddish tints being the most common. Pure white lumps, which are plentiful in some deposits, can be used as white pigment, the method of preparation being simple, viz. merely reducing the mass to powder. This is easily effected, the specific hardness of gypsum being only 2 ; and in many cases it is soft enough to scratch with the finger-nail.

If the original gypsum is white, the powder forms a dazzling white flour which, notwithstanding, is of comparatively little value as a pigment, on account of its low covering power. For this reason, powdered gypsum is chiefly used for making plaster of Paris (calcined gypsum) for plaster casts and stucco. Gypsum may also be employed to advantage for lightening various colours, since it is inert towards even the most delicate.

Kaolin, Pipeclay

Large areas of the earth's surface are covered with clay, which often attains a considerable thickness.

Nevertheless, the kind of clay that is suitable for use as pigment is comparatively scarce. The principal requirement for this purpose is a pure white colour, but by far the great majority of clays are either yellow or of a shade between blue and grey (for example the clay of the Vienna basin).

The character of clay is just as varied as its colour. In some places, large deposits of extremely fine clay are found, the material, when mixed with water, forming a highly plastic mass which, when dried and subjected to slight pressure, furnishes a very soft powder. On the other hand, some clays are so interspersed with large quantities of sand, large stones and the debris of mussels, that they cannot be used until they have been put through very careful mechanical treatment.

This great divergence in the physical character of clays is due to their method of formation. Clay originated in the weathering of felspar, which chiefly consists of a double salt, a compound of the silicates of alumina and potash. Under the influence of air and water, this compound is decomposed, the potassium silicate passing into solution, whilst the aluminium silicate, being insoluble in water, is carried away by that medium. When the water can no longer carry the particles of aluminium silicate in suspension—for example when it reaches a sea or lake—the silicate settles down to the bottom, and a deposit of clay is formed.

If the original felspar was very pure, and in particular very low in iron, the resulting clay will be of a handsome white colour. An example of this is afforded by kaolin, or porcelain earth, which is preferably used for making china. If, however, the felspar contained a

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considerable proportion of ferric oxide, the resulting clay is yellow; and if stones or mussel shells became incorporated with the clay prior to deposition, these bodies will be found as inclusions in the deposit, and such clay will require much troublesome preparation— grinding and levigation—before it is fit for use.

For the purposes of the colour-maker, the most suitable clay is one that is pure white, free from inclusions, and does not change colour when exposed, in a finely divided state, to the action of the air. Many clays that were originally white gradually assume a yellow tinge on prolonged exposure to air and moisture, because the clay contained ferrous oxide, which changes, in the air, to the stronger pigment, ferric oxide.

Many kinds of clay merely require a simple levigation to fit them for use as pigment. The lumps of freshly dug clay are placed in large tanks, etc., filled with water and stirred up continuously in order that, instead of forming a plastic mass which is very difficult to distribute in water, the particles detached from the lumps may pass at once into suspension. This turbid water is then transferred to another tank, etc., where the minute particles of clay are allowed to settle down, and the water becomes quite clear.

Where this work is carried on on a large scale, it is advisable to put the freshly won clay into large pits close to the clay deposit, and to leave it there, covered with water, during the winter season. The freezing of the water breaks down the larger lumps of clay, by the resulting expansion, and this facilitates the subsequent levigation, the cohesion between the particles being destroyed.

If the clay contains larger proportions of lime or

magnesia, a little experience will enable their presence to be detected at once by the way the clay behaves on being placed in contact with water. Pure clay quickly forms a fatty and extremely plastic paste, and sticks closely to the tongue when applied in the dry state. On the other hand, clay containing much lime or magnesia is far less plastic when mixed with water, and the dry clay hardly adheres to the tongue at all.

These latter clays are classed as poor or lean, in contrast to the fat, plastic kinds. For certain purposes for which clay is used as pigment, these admixtures are not harmful; whereas others, especially quartz sand and mica, not infrequently present in white clays, constitute a serious drawback.

As already mentioned, clay is formed by the weathering of felspar, which is a constituent of granite and gneiss, both rocks composed of quartz, mica and felspar. When the clay has been derived from the weathering of such rocks, it is easy to understand that it may contain admixtures of quartz and mica, which are frequently visible to the naked eye, or at any rate under the microscope. Whereas clay forms a white, amorphous mass, the grains of quartz sand are decidedly crystalline, transparent and of vitreous lustre; the scales of mica, on the other hand, appearing as thin tabular crystals, mostly of a green or brown colour and exhibiting, when viewed at certain angles, a brilliant metallic sheen.

Quartz sand can be eliminated from clay without any special difficulty, quartz being of higher specific gravity and therefore settling down quickly, leaving the delicate particles of clay in suspension in the liquid. The scales of mica are harder to get rid of, their tabular form retarding deposition from the suspending liquid;

and on this account, several washings are often required to separate them completely.

In all cases where clay is to be used as a white distemper, the presence or absence of lime is immaterial; but where it is to be employed for removing grease, lime is a drawback. This is also sometimes the case when the clay is wanted for the purposes of the colour manufacturer. The author has found, by experience, that perfectly pure, white clay forms a good paint, in a vehicle of oil or varnish—a purpose to which it has, so far, been seldom applied, if at all. Such paint is of good covering power, and possesses the valuable property of remaining quite unaffected by atmospheric influences.

If, however, the clay contains even but a small quantity of lime, it cannot possibly be used as an oil or varnish paint, for though the freshly made paint has a very good appearance, its character soon changes, turning viscous and suffering a considerable diminution of covering power. Thinning with turps or boiled oil results in the formation of small lumps, so that it is quite impossible to obtain a uniform coating on even a small surface.

This behaviour is apparently due to the presence of the lime, the explanation being that the fatty acids always present in the oils and varnishes used for the paint combine with the lime to form compounds which, from the standpoint of the chemist, must be regarded as soaps. The small lumps already mentioned really consist of lime soap, and the formation of these colourless compounds accounts for the lessened covering power.

Given a fine white clay, otherwise capable of forming a valuable pigment, it is sometimes possible, by simple

means, to eliminate accompanying lime, provided the amount of the latter is not too great, and also provided that very cheap hydrochloric or acetic acid is available. The acid need not be pure, and the impure but very strong pyroligneous acid, which is very cheap on account of its empyreumatic smell, may be used.

To eliminate lime from the clay, the still moist levigated mass is introduced, in small quantities, into a vat containing the requisite quantity (see later) of hydrochloric or acetic acid, the addition being continued until the liquid gives only a faintly acid reaction with blue litmus paper. When the clay is run in, effervescence is produced by the liberation of the carbon dioxide displaced by the stronger acid employed.

The amount of lime present in a clay may be determined by very simple means. A small sample of the clay is dried by artificial heat, until of constant weight, and exactly 100 parts by weight of the dry mass are placed in a glass and suffused with hydrochloric acid, sufficient of the latter being used to make the liquid still strongly acid after effervescence has ceased.

The contents of the glass are transferred to a filter, and washed with pure water so long as the washings continue to redden blue litmus paper. The residue is then dried until of constant weight, and the difference between the initial and final weights will give the percentage of substances soluble in hydrochloric acid.

After performing this simple test on a clay, it is easy to calculate the quantity of acid needed to extract all the soluble constituents from a given weight of the material. All that is necessary is to measure the volume of acid required to extract a small quantity

of the clay completely. Thus, if one pint of the acid at disposal is sufficient to treat one pound of the clay, the amount needed for a given quantity of clay is a simple matter of calculation.

Since, on account of the cost of pure hydrochloric acid, crude acid will always be used, it will be necessary to remember that this crude acid always contains ferric oxide in solution—this being the cause of its yellow colour. If the amount of acid taken is barely sufficient to combine the whole of the lime, leaving the latter slightly in excess, the ferric oxide—which would otherwise tinge the clay yellow—will be precipitated.

If, on the other hand, the acid is in excess, the clay is obtained free from all constituents soluble in the acid. The purified clay must then be freed from the calcium chloride, formed by dissolving the lime, by a thorough washing, since the clay would otherwise always remain moist on account of the hygroscopic properties of the chloride in question. Moreover, any small residuum of free acid would constitute a drawback on the clay being mixed with other colours.

Calcium chloride is very soluble in water, and therefore can be completely removed from the clay by washing. The purified clay is left to settle down as completely as possible, and after drawing the liquid off from the sediment, the latter is suffused with pure water and left to settle once more. As a rule, two such washings will cleanse the clay of calcium chloride and free acid sufficiently to render the product suitable for any purpose.

When large quantities of clay have to be treated in this manner, considerable amounts of calcium chloride solution will be obtained, which can be advan-

tageously utilised for the production of precipitated chalk, all that is necessary being to collect the liquor in a large tank and treat it with a small quantity of slaked lime, to transform the surplus free acid into calcium chloride and precipitate the ferric oxide present in solution. At the end of a few days the liquor in the tank will consist of a very pure solution of calcium chloride which will furnish an excellent precipitated chalk when treated in the manner already described under that heading.

BARYTES, OR HEAVY SPAR

This mineral—chemically, barium sulphate, $BaSO_4$—occurs native, as extensive deposits, in many places—England, Bohemia, Saxony, Styria, etc. It sometimes forms handsome tabular crystals, but more frequently compact masses, which may be pure white, grey yellow, etc., in colour, and are distinguished by high specific gravity (usually 4·3–4·7), to which the mineral owes its name. This high density also limits the application of the mineral, and it cannot be used as a pigment, in the true sense of the term, being only suitable as an adjunct to artificially prepared colours.

The employment of barytes in the colour industry is often regarded as adulteration, which, however, it is not when the case is considered from the right point of view. For instance, the only preparation which can properly be termed white lead consists of basic lead carbonate. This, when pure, is a rather expensive pigment, whereas, for certain purposes, the consumer requires a product that can be obtained at a low price. In order to satisfy this demand, the only course open to the colour-maker is to mix the white lead with a

cheap white substance, which enables him to turn out different grades of white lead, which, although low in price, are far inferior to the pure article in covering power. Pure white lead being itself a very heavy substance, the only bodies suitable as adjuncts are such as are also of high specific gravity; and of all the cheap pigments known, heavy spar is the only one endowed with this property. Consequently, this substance is extensively used in making the cheaper grades of white lead and the pale kinds of chrome yellow.

The only cases in which the addition of heavy spar to a colour can be regarded as an intentional fraud on the consumer is when he is sold, as pure white lead, chrome yellow, etc., a product really composed of a mixture of such colour and barytes. Moreover, the presence of barytes in white lead can be easily detected by a simple examination, pure white lead readily dissolving, with considerable effervescence, in strong nitric or acetic acid, whereas barytes is insoluble in all acids, and therefore remains, as a heavy white powder, at the bottom of the vessel. In this way both the presence and amount of barytes contained in a sample of white lead or chrome yellow can easily be ascertained.

The preparation of barytes for the purposes of the colour-maker is entirely a mechanical operation. The barytes, which though fairly hard is easily reduced, is crushed with stamps, ground in a mill and finally levigated, it being impossible to obtain a sufficiently fine powder even by repeated grinding.

Native barytes must not be confounded with the artificial barium sulphate sold as permanent white or blanc fixe, which is an extremely finely divided

barium sulphate obtained by precipitating a solution of a barium salt with sulphuric acid or a soluble sulphate, and is a painters' colour that is highly prized for certain purposes. Both the native sulphate and the artificial variety have the property of remaining completely unaltered by exposure to air, and they can therefore be mixed with any kind of pigment without fear of the colour deteriorating.

As a rule, barytes is first roughly crushed in edge-runner mills or stamps, and then ground to the extreme degree of fineness obtainable in ordinary mills. Even with the greatest care, however, it is impossible by this means to obtain sufficient fineness of division for mixing with fine colours, the only way in which this can be accomplished being by levigation.

Given a fairly pure white barytes to begin with, levigation furnishes a handsome white pigment that can be mixed with colours of any kind; but when used by itself in association with oil or varnish, its covering power is very low and the colour never perfectly white. Native barytes is therefore unsuitable, as such, for paint.

Varieties that are not pure white are sometimes corrected with ultramarine, added in the grinding-mill. If the yellow tinge is due to iron compounds, this can often be remedied by treating the finely ground material with hydrochloric acid, which dissolves them out, this treatment being followed by a thorough washing with pure water.

As already mentioned, white lead is most frequently mixed with barytes, this being usually added when the white lead is being ground, by feeding the two materials to the mill and grinding them together.

The crudeness of mechanical methods of reduction

is clearly exemplified by comparing the most carefully ground and levigated barytes with that obtained by artificial means. The permanent white largely used in the production of wall-paper, and quite unalterable in air, is, chemically speaking, identical with native barytes, viz. barium sulphate. The two also seem to be identical in crystalline habit, as is usual in the case of one and the same mineral, whether native or prepared by artificial means. Artificial barytes is obtained by treating a soluble salt of barium with sulphuric acid, or a solution of sodium sulphate (Glauber salt), so long as a precipitate continues to form.

This precipitate is barium sulphate, which subsides completely on account of its extreme insolubility, this being greater than that of any other salt known. The rapid rate of deposition results in the formation of extremely small crystals, which, being colourless and reflecting the light completely, appear to be perfectly white. Even when permanent white is applied in very thin layers to any surface, its covering power is very considerable, by reason of the extremely fine subdivision of the material.

This behaviour of artificial barytes in comparison with that of the natural product, affords an important hint in connection with the preparation of earth colours, namely, that in order to obtain products of specially good quality, the endeavour should be to reduce the raw materials to the finest condition possible. This result is accomplished most securely by bestowing the greatest care on grinding and levigation ; and it is therefore highly important that the manufacturer should select, from the various apparatus used in reducing the materials, those that are best adapted for the purpose.

Carbonate of Magnesia

Although carbonate of magnesia is seldom used alone as a pigment, it can be advantageously employed as such when circumstances permit. It is met with not infrequently, in Nature, in a crystalline form, as magnesite or bitter spar, the latter name arising from the fact that the soluble salts of magnesia have a bitter taste. Still more frequently, magnesia occurs in association with calcium carbonate, in the mineral dolomite, which contains up to 20% of magnesia.

A less abundant native mineral is hydromagnesite, which consists of basic magnesium hydrocarbonate. Hydromagnesite is a very light, chalk-white mass, with a non-greasy feel, which, when reduced to a soft powder, forms an excellent material for paint. It is highly inert, in a chemical sense, and can therefore be mixed with the most delicate colours, having no other effect thereon than to render them lighter in shade.

This product can also be prepared artificially, by treating a dissolved magnesium salt with a solution of carbonate of soda, the result being the formation of a pure white precipitate, which is very brilliant when dry, and is characterised by unusually low specific gravity. In some places, conditions are such that this preparation can be made on a large scale at very low cost. For instance, there is a spring at Bilin, in Bohemia, the water of which contains large quantities of alkali carbonates in solution ; whilst in the vicinity of Saidschütz is a spring fairly rich in magnesia salts. The waters from these two springs are concentrated by evaporation, and mixed in large tanks ; and when a sufficient deposit of the resulting basic carbonate of

magnesia has accumulated, it is taken out of the tanks, placed on linen filters and washed with water. The residue is dried slowly, without the employment of a high temperature, and then forms a white powder, which is very light and can be used for a number of purposes, chiefly medicinal, though it is also well adapted as a material for paint.

For this latter purpose it is, however, far too expensive; but since the conditions obtaining at Bilin are certain to occur elsewhere, we have included carbonate of magnesia among the earth colours.

On account of its specific lightness, carbonate of magnesia is specially adapted for making pale shades of certain delicate lake colours, which, if toned with even perfectly pure chalk, would undergo alteration in course of time. Carmine, for instance, can be graded, by the addition of carbonate of magnesia, into every possible variety of shades between the pure red of carmine itself and the palest pink; and the resulting colours are quite permanent whether mixed with gum solution or any other vehicle.

TALC

Although this mineral is not used as a pigment by itself, it must be mentioned here because it is not infrequently employed for mixing with other colours, and is also used in the wall-paper industry. It also serves to distribute certain pigments in a state of fine division, the " rouge végétal " of the perfumer, for example, usually consisting of talc and a small quantity of very fine carmine.

In commerce the name talc is sometimes applied to two separate minerals, true talc and steatite or soap-

stone. The former is rarely met with native as well-defined crystals, mostly occurring as scaly masses in primitive rocks. Thin pieces exhibit a certain degree of flexibility. The hardness of this mineral is so small that it can be scratched with the finger-nail; and its sp. gr. is 2·9–2·8. Talc is easily scraped, and the powder remains sticking to the knife, a property which renders the substance difficult to reduce to powder, because it balls together and takes a very long time to convert into a fine flour. The process is facilitated by calcining the talc and quenching it in cold water, this treatment increasing the hardness and at the same time making it more brittle, and thus more easy to pulverise.

A characteristic feature of all the talc minerals is their peculiar greasy appearance and feel. The colour varies, white pieces alone being of any use to the colour manufacturer. The yellow- or green-tinged varieties owe their shade to the presence of ferric and ferrous oxides. In chemical composition, talc consists of a combination of magnesium sillicate with hydrated silica, the supposed formula being : $4MgO \cdot SiO_2 + H_2O \cdot SiO_2$, and the percentage composition : silica, 62·6% ; magnesia, 32·9% ; water, 4·9%.

STEATITE OR SOAPSTONE

Steatite so closely resembles talc in most of its properties, that the two minerals were long regarded as identical. Whereas, however, talc is scarcely acted upon at all by the strongest acids, steatite is completely decomposed by prolonged boiling therewith, although both minerals have exactly the same composition.

As a pigment, steatite is far more important than talc, and, as French chalk, is largely used for drawing

or writing.   To prepare it for this purpose pure white steatite requires no preliminary treatment, beyond cutting the large lumps up into quadrangular prisms, which are mounted in wood, like lead pencil, and used for writing on the blackboard.   The powder produced in the cutting process is made up into pastel crayons. With this object, the powder is mixed with a sufficient quantity of some mineral pigment to produce a mass of the desired shade, and is kneaded to a stiff paste with water containing an adhesive such as gum, glue or tragacanth mucilage.   The mass is shaped into prisms, which, when dry, are cut into pencils and mounted in wood.   Steatite being like talc, without action on even the most delicate colours, can be used as a diluent in the preparation of light shades.

CHAPTER V

ALL the yellow earth colours, without exception, have ferric oxide as their colouring principle, the differences in shade being entirely due to the varying proportion in which that oxide is present. The various names under which they are known date back to a period when the chemical nature of these colours was still unknown, and have been mostly derived from the locality of origin.

The yellow earths can therefore be divided into two groups, according to their chemical character. The first group, in which the ferric oxide is present as hydroxide, comprises all the ochres, Siena earth, and a number of others which are obtained from native ochre by special treatment. In the colours of the second group, ferric oxide is still the colouring principle, but is combined with other substances in place of water.

It is, as a matter of fact, incorrect to rank the ochres in general as yellow earths, because they can be made to yield nearly every variety of colour from the palest yellow to the deepest red, brown and violet. These colours merit the particular attention of the colour-maker and the painter, being distinguished by very low cost of production, unusual permanence and beauty of tone. In the interests of that highly important matter to the artist, namely the production of colours

of unlimited permanence, it is desirable that colour manufacturers should bestow greater care on the manufacture of these colours than has hitherto been the case. An extremely favourable point about nearly all these pigments is that they can be very cheaply prepared by artificial means, so that the manufacturer is in a position to turn out a large number of the handsomest and most durable colours with a small amount of expense and labour.

THE OCHRES

Ochres are found in many localities, most frequently in stratified rock and rubble. The deposits are rarely extensive, mostly occurring in pockets or beds. Wherever found, ochre may be termed a secondary product, that is to say, one that has been formed through the destruction of other minerals. The analysis of ochres from different deposits shows great divergence in composition; and some consist almost entirely of pure ferric hydroxide, that has already undergone natural levigation and can be used as a pigment as soon as dug.

Such a form is, however, rare, and most ochres are intermixed with smaller or larger amounts of extraneous minerals, the contamination being sometimes so great as to preclude the use of the ochre as pigment by reason of the high outlay required for extracting the colouring constituents.

Occasionally, the ferric hydroxide is associated with a certain proportion of clay, and as this increases, the ochre passes over into ferruginous clay. This class can also be used as pigment, in certain circumstances, that is to say when it is sufficiently rich in ferric oxide to furnish a deep red mass on calcination. When,

however, the proportion of ferric oxide is low, its pigmentary power is no longer sufficient, and the clay has not the requisite beauty of colour. The ordinary earth used for making tiles is an example of this class, its colour in the raw state being an ugly brownish-yellow, but turning a dull " brick " red when fired.

In some deposits the ferric oxide is accompanied by lime. Unless the latter exceeds a certain proportion, such ochres, too, are suitable as pigments, the lime being easily removed by simple levigation; but when the amount of lime is high, it is difficult to obtain certain highly coloured shades of ochre from such material. These shades entail the calcination of the ochre, and the temperature required is oftentimes insufficient to transform the lime into the caustic state. Moreover, the presence of caustic lime would be a drawback in some cases, it being then impossible to mix the ochre with other colours without endangering the shade through the action of the lime on these latter.

The following analyses will show the percentage composition of ochres from various deposits :

Ochre from—

	Comoal (Savoy).	Vierzen.	St. Georges.
Ferric oxide . . .	19	23·5	25
Lime	2	—	—
Alumina	20 ⎫		
Magnesia	1 ⎬	69·5	70
Silica	44 ⎭		
Water	7	7	5

In the majority of cases the mineralogical characteristics of an ochre enable conclusions to be formed as to its suitability as pigment. Good ochre is more or

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less yellow to dark brown in colour, and can easily be crushed between the fingers to a soft, fine powder which feels like powdered steatite and does not produce a sensation of grittiness, this latter indicating the presence of fine grains of sand in the ferric oxide. The behaviour of the ochre in presence of water is specially important. If it adheres firmly to the tongue, and forms a fairly plastic paste when mixed with a little water, the mineral contains a large percentage of ferric oxide, and as a rule will yield ochre of good colour.

In general it may be said that the value of an ochre varies directly with its content of ferric hydroxide or oxide, because when this is large the ochre will furnish a wide range of colours under suitable treatment.

A simple test for quality consists in weighing out an exact small quantity (10 grms.), and heating it to a temperature not exceeding 110° C., until the weight remains constant. A simple calculation then gives the amount of uncombined water in the sample. Since the proportion of such water varies in different parts of one and the same deposit, the test must be repeated, in order to obtain accurate results, on samples taken from different points, or, preferably, on a properly prepared average sample.

Even drying changes the colour of ochre considerably. To ascertain the behaviour of an ochre on calcination, a large sample is dried at 110° C. until the weight is constant, and divided up into a number of small samples weighing, say, 10 grms. each. The samples are then heated to different temperatures, one to the melting-point of lead, another to that of zinc, and so on.

The higher the temperature employed, the more will the colour of the ochre approximate to red; and specimens very rich in ferric oxide will give bright red

colours. Beyond this range, a further increase in temperature will give violet shades, varying with the temperature and the duration of heating. After this preliminary test, it is desirable to make another on a larger scale, with quantities up to about 1 lb. For this test, the different kinds of ochre frequently found in the same deposit should be mixed together, in order to obtain an idea of what the mean product, obtained in working on the large scale, will be like.

On the whole, the results of this second test will be the same as in the first series, the only object of the second test being to gain information which may be particularly valuable in practical work. The bottles in which the calcined samples are stored should be marked with the temperature and length of heating, so that, when it is subsequently desired to obtain an ochre corresponding to a particular sample, all that is necessary will be to heat it to the same degree from the same length of time. The performance of this simple test will be of great assistance in standardising the work with a minimum loss of time.

When it is desired to ascertain the composition of an ochre superficially its behaviour towards hydrochloric acid may be noted. A weighed quantity of the freshly dug (undried) ochre is treated with pure acid, free from iron, which will dissolve out the ferric oxide and lime, leaving clay and quartz sand behind. The presence of lime is indicated by effervescence on contact with the acid; and if there is no effervescence, lime is absent. At the end of several hours the acid is carefully decanted from the undissolved residue which is then stirred up with water, left to subside, and weighed when dry. This method will give the amount of substances, other than ferric oxide and lime, in the

sample. These substances usually consist of clay or sand.

For a quantitative determination, a small quantity —usually 1 grm.—is weighed out, treated with a corresponding amount of hydrochloric acid, and the solution filtered into a glass. The residue on the filter is washed with distilled water, the washings being united to the acid solution.

This solution is treated with ammonia so long as a precipitate of ferric hydroxide continues to form, this being collected on a tared filter and dried at 110° C. The precipitate may be regarded as pure ferric hydroxide, and its weight will indicate the proportion of hydroxide in the ochre with sufficient accuracy for technical purposes.

In reality, however, it is not pure ferric hydroxide, but contains in addition all the oxides that are precipitable by ammonia, lime being always carried down as well. It is therefore desirable to dissolve the precipitate with a little hydrochloric acid, and reprecipitate with ammonia.

CALCINING (BURNING) OCHRE

In many places ochre is only put through a very simple mechanical preparation before being sold for pigment, namely left to dry in the air so that most of the uncombined water evaporates. No matter how this drying process is protracted, however, it is impossible to get rid of all the water in this way, a certain proportion being retained by the hygroscopic action of the ferric hydroxide, and to expel this the mass must be heated to above 100° C. Drying is usually succeeded by pulverising and sifting the loose earthy mass, which is then ready for sale.

When the ochre contains sand or stones, this treatment is not sufficient, and levigation is necessary. No particular trouble is involved, the mineral being fairly heavy as the result of its content of ferric hydroxide. A simple method of treatment suffices to improve the value of the ochre considerably, and enables a grade that is not particularly bright-coloured in its natural condition to be converted into products of very handsome tone and various shades. This treatment consists in heating the raw ochre to a definite temperature, during which process the colour changes progressively, and any desired tone can be obtained by suddenly cooling the hot mass.

The reason for this phenomenon is that the higher the temperature, the larger the amount of water driven off from the ferric hydroxide, until finally, when a very high temperature has been reached, the whole of the water is expelled, and the ferric hydroxide is transformed into ferric oxide. The hydroxide is brown, whereas the oxide, provided the temperature has not been raised too high, exhibits the characteristic colour known as " iron red."

Consequently, the colour of moderately calcined ochre ranges through a whole scale from brown to red ; and the higher the temperature employed, the redder the tone. If the heating be protracted after all the hydroxide has become oxide, the latter undergoes molecular change, increasing considerably in density and altering in colour ; and after very prolonged heating, the colour finally becomes violet.

The calcination, or burning, of ochre is ordinarily performed in a very crude manner. The mineral is crushed to the size of peas, and spread out on an iron plate which is made red-hot. As soon as the ochre

has reached the desired shade of colour, it is dropped into a tub of water and then crushed to powder. The calcination requires great experience on the part of the operator, because so long as the product is hot, it has quite a different colour from that assumed on complete cooling. Since only comparatively small quantities of ochre can be treated in this way, and the operation unnecessarily increases the cost of the product, owing to the large consumption of fuel, it is highly desirable to employ a simple calcining apparatus capable of treating large quantities.

Such an apparatus may consist of an iron drum, mounted with a gentle slope inside a furnace, from which it projects at both ends. A shaft carrying a sheet metal worm is rotated inside the drum; and the whole apparatus is very similar to an Archimedean screw.

When the iron drum is raised to a strong red heat, and small quantities of ochre are fed continuously into the upper end of the drum, the rotation of the worm will push the material forward, and contact with the glowing sides of the drum will produce the necessary calcination, the degree of which can be modified by altering the speed at which the worm is turned. The calcined product is discharged at the lower end of the drum, either into a vessel of water, or, if only moderate heating has been applied, direct into a collector.

Fig. 28 represents an apparatus designed by Halliday for the dry distillation of wood waste; but, with slight structural modifications, it can also be used for calcining ochre. The material to be heated is introduced, in small pieces, into the feed hopper B, and is carried downward, by the worm C, into the red-hot drum A, through which it is propelled by the worm D until it

drops out, at F, into the tank G. The length of time the material is subjected to calcination depends on the speed at which the worm D is run. The pipe E carries off the water vapour expelled from the charge.

In order to obtain a uniform product when ochre is calcined in an apparatus constructed on this principle, it is necessary that the material introduced should be
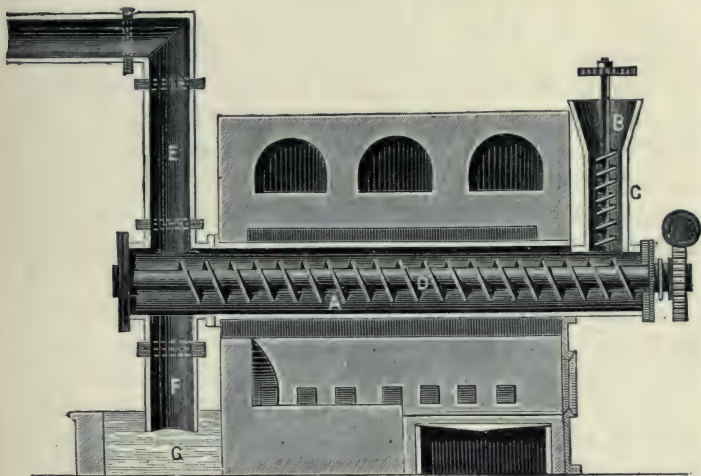
FIG. 28.

fairly regular in size, a condition which is easily fulfilled by squeezing the freshly dug ochre between fluted rollers, and then passing it over a series of screens, each grade being then calcined separately.

Moreover, the apparatus is only suitable for calcining at medium temperatures; and when highly calcined products are in question, the operation is best performed in fire-clay cylinders, or in thick cast-iron drums, similar to gas retorts, built into a furnace.

Other devices for calcining ochre will be described later.

Ochres from Various Deposits

As previously stated, ochres are frequently met with in Nature, both in the immediate vicinity of iron ore, and also at considerable distances from such deposits. In the latter case, the ochre must be assumed to be the decomposition products of ferruginous minerals and to have been carried off by water until the latter became stagnant and allowed the ochre to settle down. In their method of deposition these ochres are therefore analogous to clay, and they, too, often contain large quantities of extraneous minerals, which have given rise to the diversified substances grouped under the name of ochre.

Although ochres are so widespread in Nature, only certain kinds, found in certain localities, have acquired a high reputation. For the most part, these ochres are such as have already been prepared in a high degree, by Nature, for the purpose for which they are employed.

Thus, we find that all the ochres which have acquired a high repute among painters for particular beauty of tone and permanence, are distinguished by two properties : a high content of ferric hydroxide and great purity.

The former of these properties imparts brightness of colour; and such products will furnish, on calcination, a wide range of colour shades. When, as is the case with the finer qualities of ochre, the mineral contains only a very small proportion of impurities, there is no difficulty in bringing it, by simple grinding

or levigation, into a condition in which it is at once fit for use as a pigment.

The Italian ochres have, for long ages, enjoyed a high reputation for their beauty of colour and permanence. This category includes, for example, the renowned Siena earth, Roman earth, Italian umber, and other ochre colours. This high renown is probably due less to the inherent properties of the mineral than to the circumstance that the art of painting attained a high state of development at an early period, and that the artists paid special attention to the use of bright and permanent colours for their work.

Although, at present, many deposits of ochre are known that are quite able to compete, on the score of beauty, with the best Italian products, the good name of these latter has nevertheless been maintained. It is true that the name of Italian ochre is often merely borrowed, for application to a product originating in some other country, varieties of terra di Siena, for instance, being put on the market that have actually been derived from deposits in Germany.

As a result of this custom, certain names, such as terra di Siena, umbra di Roma, have become generic terms, and their use denotes, not an intention to suggest that the earth colours in question really come from Siena or the vicinity of Rome, but that the properties of the article are equal to those of the old-established colours of Siena or Rome.

It would occupy too much space to go into an exhaustive description of all the native varieties of ochre, and would inevitably lead to a good deal of repetition. It will therefore be sufficient, for our purpose, to deal with only a few of them.

The best-known ochres are those of Rome and Siena,

the latter being frequently called, in commerce, by its Italian name, terra di Siena.

Roman ochre forms yellowish-brown masses, of fairly fine texture and composed of ferric hydroxide and clay. They are put on the market both in the raw and calcined state. On calcination, the colour soon changes to red, and if carefully performed, the resulting colours have a very warm, fiery tone.

Closely approaching Roman earth is the English ochre, which is worked more particularly in Surrey, and is not infrequently sold as Roman. In many deposits this English ochre occurs in such a high state of purity that the best pieces are picked out and sold without being even crushed or ground. The pieces of lower quality are very carefully ground and levigated, for the purpose of being calcined for the production of different shades, and then furnish highly prized colours.

In point of chemical composition, the ochre family also includes terra di Siena, bole, umber and Cassel brown. These minerals, however, are not yellow like ochre, but brown, and will therefore be dealt with along with the brown earth colours.

Artificial Ochres

Products very similar, both in chemical composition and colour, to the native ochres can also be very simply and cheaply made by artificial means. Their preparation may be particularly recommended to colour-makers who desire to turn out a wider range of iron pigments, but are not in a position to obtain natural ochres at a low price.

In the manufacture of artificial ochre, an endeavour is made to imitate the natural processes which have

led to the formation of ochre, and, of course, to avoid anything likely to hinder the production of a suitable colour earth, for example the presence of sand or a considerable admixture of extraneous minerals.

As already mentioned, the chief impurities in natural ochres are clay and sand, both of which can be easily excluded during the manufacture of artificial ochre, or their amount controlled in such a manner that paler or darker products can be obtained at will, and the tone varied, in any desired manner, by calcination, as in the case of the native article.

The raw material for artificial ochre is always a ferrous salt, which can be purchased in large quantities and at very low prices, namely green vitriol, which, in the pure state, consists of ferrous sulphate, $FeSO_4$ $+ 7H_2O$. This substance forms sea-green crystals, which are readily soluble in water and impart an objectionable inky flavour thereto. On exposure to the air, green vitriol turns an ugly brown colour, and is no longer completely soluble in water, passing gradually into the condition of basic ferrous sulphate. This is because ferrous oxide is a highly unstable substance, which attracts oxidation and changes into ferric oxide. This latter, however, requires for the production of soluble salts a larger quantity of acids than does ferrous oxide, and therefore the oxidation of ferrous sulphate in the air leads only to the formation of salts that are imperfectly saturated with acid, namely basic salts.

When a solution of green vitriol is left exposed to the air, basic ferric sulphate is also formed, which settles down to the bottom of the vessel as a rusty powder. If, however, a corresponding quantity of sulphuric acid be added to the solution at the outset, the resulting ferric sulphate remains in solution.

On treating the green vitriol solution with one of caustic potash, caustic soda or quick lime, the ferrous oxide is thrown down as the corresponding hydroxide, forming a voluminous greyish-green precipitate. This hydroxide still possesses a great affinity for oxygen, and when the precipitate is brought into contact with air, its colour rapidly changes to a rusty red, through the transformation of the ferrous hydroxide into ferric oxide. The ferrous hydroxide can also be precipitated by alkali carbonates, the deposits behaving in exactly the same manner as that thrown down by the caustic alkalis.

Various methods can be adopted in the preparation of artificial ochre, the selection depending on the properties desired in the finished product. To obtain an ochre with particularly good covering power, the method must be different from that employed to furnish a cheap product, in which low price is more important than covering power.

In the former case, the ferrous hydroxide is mixed with substances which, in themselves, possess fairly high covering power, such as chalk or white clay; in the second, gypsum, which is of low covering power, is used.

The preparation of the cheapest kinds of artificial ochre will be described first, followed by that of the higher grades which belong to the most valued artists' colours.

For cheap artificial ochres, the ferrous hydroxide is thrown down by caustic lime from a solution of green vitriol. According as a lighter or darker shade is required, two to three parts of ferrous sulphate are dissolved in water, care being taken to select crystals of a pure green colour, since those that have a rusty

look are only imperfectly soluble, because they contain basic ferric sulphate.

The solution will always be cloudy, owing to the partial precipitation of the hydroxide by the lime in the water; but this is immaterial. For the precipitation, a milk of lime is prepared by slaking one to two parts of quicklime (according to the quantity of ferrous sulphate to be treated) in water, and stirring this up in enough water to make a thin milk. Care must be taken to exclude any large particles of lime, since these would find their way into the finished product and make the colour uneven. On this account, the milk of lime should be carefully strained through a loosely woven cloth or fine sieve, into the precipitation vessel.

The ferrous sulphate solution is then poured in, the mixture being kept stirred, and an ugly, grey-green precipitate is produced, consisting of a mixture of ferrous hydroxide and calcium sulphate, the reaction being explained by the equation :—

$$FeSO_4 + Ca(OH)_2 = Fe(OH)_2 + CaSO_4.$$

The larger the amount of ferrous sulphate solution added to the milk of lime, the darker the resulting ochre. As soon as all the ferrous sulphate is in, the stirring is suspended, and the liquid is left until quite clear. The water is drawn off through tapholes in the side of the vessel, care being taken not to disturb the fine precipitate, and fresh water is added, in which the deposit is stirred up and again left to settle down. This operation, which is once or twice repeated, is to wash the precipitate.

When this object has been sufficiently accomplished, the mass is shovelled out of the vessel and spread

thinly on boards, where it is left until the desired shade
of colour has been attained, the colour changing quickly
on exposure to air, owing to the oxidation of the ferrous
hydroxide into ferric hydroxide.   To ascertain whether
oxidation is complete, a large lump of the mass is
broken across; and if it is of a uniform yellow-brown
colour throughout, without being darker on the outside
than in the middle, all the ferrous hydroxide will have
been transformed into the ferric state.   The product
can now be dried at once, and when ground will be
ready for sale.

To obtain different varieties from the product, it
is carefully heated (in a finely powdered condition) in
shallow pans; but the operation needs caution, or the
water in the gypsum present will be expelled, giving
rise to drawbacks that are manifested when the colour
is used.

For instance, in mixing such a colour with water,
the gypsum would again absorb water and cause the
whole mass to set as a useless solid lump.   Since
gypsum parts with its water at a comparatively low
temperature, it is better not to heat these cheap ochres
at all, but to obtain the various shades by modifying
the proportion of ferrous sulphate employed.

Another defect of the ochres prepared by this method
resides in the excess of lime present, it being impracti-
cable to measure out the quantity of lime used with
such accuracy that only just enough is taken to pre-
cipitate the ferrous hydroxide, there being always a
slight excess.   This lime is transformed into calcium
carbonate on the mass being exposed to the air, just
as in the preparation of Vienna white; but as the
saturation with carbon dioxide takes a considerable
time, some of the lime remains in the caustic state

and is liable to affect other colours that may be mixed with the ochre.

An artificial ochre uniting in itself all the qualities of the natural product, and also capable of being shaded by burning, can be prepared in the following manner. An accurately weighed quantity of pure crystallised ferrous sulphate is dissolved in a definite amount of water, and the solution is treated with successive small portions of crude nitric acid, until all the ferrous oxide has been changed into the ferric state. The change can be detected by a very decisive test. If a liquid containing ferric oxide in solution is brought into contact with a solution of red prussiate of potash (potassium ferricyanide), no precipitate is formed in the absence of ferrous oxide, but only a brown coloration; whereas, if ferrous oxide is present, a beautiful blue precipitate is formed at once, the colour of which is so intense that very small quantities of ferrous oxide can be detected by this means.

For the purpose now under consideration, the presence of small amounts of ferrous oxide in the solution is immaterial, because they are soon changed into ferric oxide on exposure to the air. It might, therefore, be asked, why take the trouble to oxidise the ferrous oxide by means of an agent involving expense, which could be saved by allowing the oxidation to take place in the air?

The advantage, however, of the direct employment of a solution of ferric oxide is that it gives at once a colour that can be dried straight away; whilst at the same time the colour undergoes no change in drying, whereas it does when ferrous oxide solution is used.

The method of producing ochres from this ferric solution varies according as the product is to be used

without any further treatment than drying, or is to be modified by firing.

In the former event, caustic lime is again used as the precipitant, but in only just sufficient quantity to throw down all the ferric oxide in the solution. This amount can be calculated exactly, 36·84 parts by weight of pure burnt lime being required for every 100 parts of pure ferrous sulphate taken. The actual quantity, whether larger or smaller, will depend on the relative purity of the sulphate and lime; and this can readily be ascertained by a simple trial.

The lime is used in the form of milk of lime, as already described. If lime alone is employed, the precipitate will consist of pure ferric hydroxide and the calcium sulphate thrown down at the same time. The resulting colour, when dried, will be an intensely brown mass, which can be used in place of the very dark natural ochres.

In order to obviate entirely the disadvantages resulting from the presence of a large amount of caustic lime in the precipitate, fine levigated chalk or white clay is added in the preparation of the lighter shades of ochre, the addition being made as soon as the two ingredients have been brought into contact; and the mixture is thoroughly stirred, to ensure uniform admixture with the ferric hydroxide. The colour of the settled deposit will be lighter or darker in proportion to the amount of chalk or clay employed; and in this way the whole range of shades from pale yellow to bright brown can be obtained without the application of heat.

Ochre that has been made with chalk is unsuitable for toning by heat, because this treatment would causticise the lime, and the ochre could not be mixed

with other colours, since these would be affected by that substance. On the other hand, when white clay is used in preparing the ochre, the latter can be more easily toned by firing, provided care be exercised in the process. The ochre must be dried completely in the air, and either spread out in thin layers on iron plates, for the burning process, or else put into a drum, of the kind already described, in which the mass is moved onward by a worm.

The clay remains unaltered in firing, but the gypsum parts with its water of crystallisation. In order to restore the latter, the ochre issuing from the drum is discharged direct into a vessel of water, in which it can be kept in constant motion by a stirrer. The water is soon warmed by the heat of the mass, and absorption by the gypsum proceeds at a rapid rate. When the whole charge has been fired and collected in the vessel of water, the stirrer is stopped and the precipitate dried, being then ready for use.

In certain circumstances, ochre can be made by other methods. In large towns, ammonium salts are sometimes obtainable at a moderate price, being manufactured in large quantities as a by-product in gasworks. For our purpose, crude gas liquor might be used, since it contains ammonia for the precipitation of the ferric hydroxide. In most cases, however, this gas liquor contains only very small quantities of ammonia, and, therefore, in a works of any size, very large vessels would be needed for the production of a comparatively small quantity of ochre. On this account, preference is given to crude carbonate of ammonia, which is also obtainable at low prices.

On bringing a solution of this salt into contact with one of ferric oxide, ferric hydroxide is precipitated,

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and the sulphate of ammonia resulting from the reaction remains in solution. By stirring white clay into the liquid at the same time, the ochre can be correspondingly lightened in shade.

The precipitates obtained in this way can be dried at once, and converted into any shade obtainable with natural ochre, from brown to red, by strong firing. The sulphate of ammonia still remaining in the air-dried product is completely volatilised by the heat, and the resulting ochres are even superior to the natural varieties in beauty and permanence.

Ochres as By-Products

In the manufacture of certain chemicals, substances of divergent composition are obtained which are sold under the name of ochre and are used as painters' colours. Whereas ochre, properly so-called, consists of either ferric hydroxide or ferric oxide in association with clay, lime, etc., the products now under consideration are basic ferric salts composed of varying quantities of ferric oxide in combination with certain proportions of sulphuric acid.

These ochres are obtained as by-products in the manufacture of green vitriol from pyrites, and in alum manufacture; and, according to their origin, they are classed as vitriol ochre, so-called alum sludge, and pit ochre. All the basic ferric sulphates of which they are composed form fairly large crystals, and, therefore, in most cases, the covering power is small. On this account the products are of low grade and are put on the market at low prices, for which reason they are largely used in making cheap paints.

Vitriol Ochre.—Commercial green vitriol is, for the

most part, manufactured from native sulphides of iron. When many of these sulphides are piled in heaps and left to the action of the air, oxygen is gradually absorbed and green vitriol is formed which is dissolved out by rain and is collected in large clarifying tanks.

In the case of pyrites, however, the mineral must first be roasted in a current of air, since otherwise its conversion into green vitriol would only proceed in a very sluggish manner. In any event, the aqueous solution of ferrous sulphate has to be concentrated, by evaporation, to the point at which the green vitriol crystallises out.

Both in the clarifying-tanks and—still more so—in the evaporating-pans, a rusty-looking sediment forms at the bottom, consisting of basic ferric sulphate. This originates in the partial oxidation of the ferrous oxide (first formed) while the pyrites is exposed to the air, and since the quantity of sulphuric acid present is insufficient to saturate all the ferric oxide, basic salts are produced.

The yellow-brown sludge deposited in the pans during the concentration of crude green vitriol liquor, constitutes the product termed vitriol ochre, which contains varying amounts of ferric oxide, sulphuric acid and water, according to the quantity of ferric oxide resulting from the oxidation of the pyrites and the character of the latter, e. g. :—

Ferric oxide	.	.	.	.	65–70%
Sulphuric acid	.	.	.	.	14–16%
Water	.	.	.	.	13–16%

Although the colour of these ochres is not particularly handsome, they can be transformed, by firing, into colours of fairly good quality. As this subject will be

more thoroughly gone into when dealing with the preparation of the red iron pigments, the applicability of these ochres will only be casually referred to here. During the burning process, these ochres, of course, part with the whole of their contained water; and by protracted, high calcination, the whole of the sulphuric acid can also be expelled, so that finally nothing but pure ferric oxide is left.

Alum Sludge.—Solutions of crude alum always contain a certain amount of ferric oxide which settles down at the bottom of the pans during concentration. This sludge, too, consists of basic ferric sulphate, but is inferior in covering power to vitriol ochre, the crystals being of coarser grain. On the other hand, the ochreous sediment from the alum concentrating-pans has the valuable property of being readily transformable into red-brown to pure red tones by burning. For this reason, particular attention has been devoted to this sludge in a number of alum works.

Since the products are only of value when burned, and the shades thereby obtained are always red, they will be dealt with more fully along with the red earth colours.

Pit Ochre.—Springs containing small quantities of ferrous sulphate and other salts are met with in many iron mines, but, in most cases, the amounts are too small for their recovery by artificial concentration to be contemplated. If, however, the conditions allow of the springs being easily diverted, they may often be utilised for the preparation of low-grade ochre.

The chemical composition of these pit ochres varies considerably, and depends on the geological character of the locality. Water can only dissolve such minerals as occur in the form of fairly readily soluble com-

pounds; and for this reason pit waters are always
solutions of the metals which are found in the mine.

The variety of compounds that may be present in an
ochre can be seen from the subjoined analyses of
ochres deposited from pit waters at Rammelsberg.
As elsewhere, two distinct classes of ochre are met with,
having a conchoid and an earthy fracture respectively.
The latter usually contain rather more ferric oxide,
and, in particular, a higher content of foreign sub-
stances, the most important of which is quartz sand.
In the Table, the ochres with conchoid fracture are
marked A, and those with an earthy fracture, B.

					A.	B.
Ferric oxide	.	.	.	.	68·75	63·85
Zinc oxide .	.	.	.	.	1·29	1·23
Copper oxide	.	.	.	.	0·50	0·88
Sulphuric acid	.	.	.	.	9·80	13·59
Water	.	.	.	.	15·52	18·45
Clay and Quartz	.	.	.	.	4·14	2·00

The preparation of the ochre is a simple matter,
consisting in collecting the mass and sorting out the
loose, earthy portions of a pure yellow colour from the
denser and darker parts. The former are dealt with
separately, usually by a simple process of levigation,
for the sole purpose of getting rid of the earthy matter,
quartz sand in particular.

The denser varieties require much more work, but
yield a far superior product, which, by suitable treat-
ment, can be converted into the finest grades of ochre.
The first operation consists in a very careful crushing,
and as the pieces are often very hard, they are treated
in ordinary or stamp-mills, edge-runners being also
employed with advantage.

The product reduced by any of these means is passed
through a number of sieves, to separate the fine

particles from the coarse; and the finest dust is burnt. This last treatment causes a considerable loss in weight, both the accompanying water and most of the sulphuric acid being volatilised. However, since, as already stated, all varieties of ochre can be obtained, the process is consequently very remunerative notwithstanding the loss in weight it involves.

Yellow Earth.—From the particulars given in the general description of the earth colours, yellow earth may also be regarded, to some extent, as an ochre, but one containing a large proportion of foreign substances. It might, however, be more accurately termed a clay contaminated with a considerable amount of quartz sand and a certain proportion of ferric oxide. The method of preparation is on the same lines as for ochre, but burning is never practised, nor is the treatment so careful as for the better grades of ochre, the low price of the colour making this unremunerative.

CHAPTER VI

RED EARTH COLOURS

THE number of minerals that can be directly used as red earth pigments is comparatively small, and by far the greater proportion consist of ferruginous colours, a few of which are obtained by the mechanical treatment of native iron ores or clays coloured red by ferric oxide, the majority, however, being formed by burning certain materials of another colour. To these belong nearly all the materials mentioned in connection with the ochres and the brown iron colours, together with a few by-products of the chemical industry.

In addition to the foregoing, which have ferric oxide for their pigmentary principle, is the native mercury sulphide, occurring, as scarlet, crystalline masses, under the name of cinnabar (vermilion). The only reason for including natural vermilion with the earth colours is to make the list complete, the largest proportion of this pigment being prepared by artificial methods. The product sold as " Chinese " vermilion may, in former times, have really been introduced from China into Europe, and prepared there by grinding and levigating the best-coloured lumps of the natural cinnabar; but, at the present time, all the vermilion made—in Europe at least—is from sulphur and mercury, by artificial processes, and the name Chinese vermilion is merely retained to designate a particularly fine grade.

On the basis of occurrence and chemical properties, the red earths can be classified into several groups. The first comprises natural products requiring only mechanical preparation, such as the minerals known as hematite, micaceous iron ore, Elbaite, etc., and the special modification of red ironstone termed raddle. All these minerals consist almost entirely of ferric oxide in a pure state. The mineral, bole (red chalk, terra sigillata, Lemnos earth), is chemically allied to the ochres, being, like them, composed of alumina, frequently accompanied by lime and small quantities of magnesia, but differing in that ferric oxide is always present in bole, whereas the ochres always contain ferric hydroxide.

The second group consists of the artificial reds obtained by burning or calcining raw materials, whose ferric hydroxide is more or less transformed by heat into ferric oxide, such as vitriol ochre, pit ochre and alum sludge.

Of late years the artificial earth colours have attained a high degree of importance. They are obtained in large quantities in the manufacture of sulphuric acid from green vitriol. Formerly, it is true, they were also used as pigments under the name of caput mortuum or colcothar, but were not held in much esteem; and it is only within recent times that it has been discovered that these inferior by-products can be converted into very handsome and brilliant colours, which now form important articles of commerce.

BOLE

Bole, Lemnos earth, terra sigillata, etc., is, for the most part, a product of the decomposition of highly

ferruginous minerals, and occurs, in the form of lumps, having a conchoidal fracture, in pockets or detritus. The lumps have a sp. gr. of 2·2–2·5, are Isabella brown to dark brown in colour, and give a slightly greasy-looking streak. There are two distinct varieties of bole : the one adhering firmly to the tongue, whilst the other lacks this property and, when placed in water, crumbles down to powder in emitting a peculiar noise.

The composition of the boles varies, but all of them may be regarded as alumino ferric silicates combined with water. Most of the specimens examined from different deposits contain 24–25% of water, 41–42% of silica, and 20–25% of alumina, the remainder consisting of ferric oxide with small traces of manganese oxide.

Some varieties, however, are exceptional and contain only 30–31% of silica and 17–21% of water, e. g. those from Orawitza and Sinope. Lemnos earth, the true terra sigillata, is mostly silica (66%) with 8% of water, and contains a smaller percentage of ferric oxide than the others. It is also of a distinct colour, lighter than the true boles and having a greyish or yellowish tinge.

The behaviour of the different kinds on burning is just as diverse as their chemical composition. Whilst some kinds are infusible at even the highest temperatures, and merely change into hard, red masses ; others, again, fuse at a moderate heat. This difference is due to chemical composition, those high in silica being generally less refractory than those in which alumina preponderates.

In order to render the boles suitable for painting, they are put through a somewhat different treatment than the other earth colours. The freshly dug material is first sorted, the uniformly coloured lumps of fine

texture being set apart and suffused with water, with which they form a pasty mass of low plasticity, which is kneaded by hand to make it homogeneous, and is then stirred up with more water. When the lumps have distributed in the water, the latter is drawn off into a second tub, and the residue is stirred up with fresh water, the treatment being repeated until the effluent no longer shows any signs of colour.

The liquid in which the finely divided bole is suspended is left to settle, and the bole subsides as a fine powder, which is dried to the condition of paste, pressed into moulds and dried completely.

Owing to its low content of ferric oxide, the colour of bole is not particularly bright, but is very permanent —a property equally shared by all the other ferric oxide pigments.

Native Ferric Oxide as a Pigment

In nature, ferric oxide forms extensive deposits, which, by reason of the light red colour characteristic of certain varieties of ferric oxide, are largely employed in painting. These colours may be classed among the oldest known to mankind, ferric oxide pigments having been used frequently in the most ancient paintings.

The most important varieties of ferric oxide for our purpose are: iron glance, with its modifications, micaceous iron ore and frothy hematite; red hematite, and raddle.

Iron Glance

This substance forms handsome black crystals of very high lustre, which, when small and scaly, con-

stitute micaceous iron ore. Both, when rubbed down, furnish a dark red powder of no particular beauty. Micaceous iron ore forms the transition stage into frothy hematite, or iron cream, the sole difference being that the crystals of the latter are much smaller, and the scales finer, the iron-black colour passing gradually into cherry red. At the same time, the lustre, though still high, loses most of the metallic sheen exhibited by micaceous iron ore.

Hematite

The variety known as hematite or bloodstone, sometimes occurring as shiny nodules, is distinguished by its handsome red colour. Some of the lumps are composed of long, thin crystals grouped about a common centre so as to form a globular mass. Despite its bright colour, the hardness of hematite (between 3 and 5) prevents it from being used as a pigment, the value of the product not being commensurate with the cost of reduction.

Raddle

There are numerous deposits of red ironstone, in the state of fine earth, where the operations of grinding and levigation have, to a considerable degree, already been carried out by Nature. These deposits form the mineral which, under the name of raddle, is often used as a pigment for ordinary paints. It may be considered to have originated in the transformation of red ironstone, by the natural forces that can everywhere be seen disintegrating rocks, namely water and frost, into a fine powder, which has been trans-

ported, often over long distances, by water, and has finally settled down.

In places where the process has been carried out in this manner, the raddle will be in a condition, as regards fineness of division and beauty of colour, that leaves nothing to be desired, and the material itself is ready for use as a very valuable pigment. Large deposits of this kind, however, are of rare occurrence; but there are plenty in which the ferric oxide is associated with varying quantities of clay, sand, and sometimes lime.

The conditions here are on all fours with those of clay, which, too, has been formed in a similar way. Pure clay, the so-called kaolin, is a highly valuable material, whereas ordinary loam—highly contaminated clay—is only of low value. In judging the quality of raddle as a pigment, the presence of impurities is of less account than their nature; and in some cases a very highly contaminated raddle may be worth far more, as a pigment, than one containing only very small admixtures of extraneous substances.

As stated above, the ordinary impurities in raddle are clay, lime and quartz sand. An admixture of clay, even if fairly large, is no great drawback, since the material can be used in its natural state, and also be toned by burning. Lime is less favourable, for though a calcareous raddle can be used as it is, the lime parts with its carbon dioxide on calcination, becoming changed into caustic lime and imparting to the product qualities which preclude its employment for a number of purposes, especially for mixing with delicate organic colours.

The presence of quartz sand is immaterial when the raddle is to be burned, inasmuch as sand is unaltered

by calcination. But it constitutes a drawback because it makes the fine raddle gritty and unsuitable for fine paint work. The only way to eliminate this impurity is by levigation—an expensive operation which should, as far as possible, be avoided for these native ferric oxides, because they must be sold very cheaply, and have to compete with the large quantities of oxide obtained as a by-product of the chemical industry.

The suitability of a given specimen of raddle for use as a pigment may be easily ascertained by weighing out exactly 100 grams and heating to about 120° C. The loss of weight will give the amount of water in mechanical retention. The residue is suffused with strong vinegar, and left for several days, being stirred at frequent intervals. The carbonates of lime and magnesia present will dissolve in the acid, the ferric oxide remaining untouched. The liquid is decanted, and the residue washed several times with water and dried, the diminution in weight being a measure of the carbonates in the sample. If the vinegar has turned a yellow colour, the presence of ferric hydroxide in the mineral is indicated, this hydroxide being readily soluble in acetic acid. If the residue feels gritty, it contains quartz sand, the amount of which can be found with sufficient accuracy by levigating the mass and weighing the sandy residue after drying.

Deposits occur, in many places, of a mineral similar to raddle, but formed under peculiar conditions. Thus, there are found, in the vicinity of brown-coal deposits that are rich in pyrites, earthy masses which are occasionally of a handsome red colour and consist of a variety of minerals admixed with a considerable proportion of ferric oxide.

These masses probably originated in fires in the coal

seams, whereby the pyrites became transformed into ferric oxide and basic ferric sulphate; and where the deposits are of sufficient size, they may be advantageously utilised in the production of cheap reds. In most cases, however, the minerals must be levigated, owing to the frequency with which they contain large proportions of extraneous minerals in a gritty condition.

Burnt Ferric Oxide and Ochres

It has already been stated, in dealing with the yellow ochres, that these colours can be toned by burning, part of the ferric hydroxide losing its water and changing into red ferric oxide. The more severe the burning, the larger the amount of ferric oxide formed and the nearer the colour of the product approximates to red. According, however, as the original ochre was yellow or brown, the tone of the burnt colour will lie between orange and brownish red. If the heating be pushed so far as to transform all the ferric hydroxide into oxide, the red will come more and more into prominence in proportion to the amount of hydroxide in the original material. If the product consists entirely of ferric oxide, as is the case with that obtained, as a by-product, in the manufacture of English sulphuric acid, a pure red ferric oxide (caput mortuum, colcothar, English red, etc.) will be obtained. If the heating be increased above a certain point, the pure ferric oxide will change colour, assuming a brown to violet tone according to the temperature employed.

(a) Burning in the Muffle

Since, as a rule, the quantity of material treated in the preparation of these brown, violet to black ferric

oxide pigments for the purposes of the painter on porcelain is not large, the same kind of muffle furnace (Fig. 29) as serves for making enamels can be used. The fireclay muffle M is inserted in a reverberatory furnace O, with a good draught, and is raised to a white heat. The finely powdered material to be burned is spread out evenly on plates of sheet-iron or fire-clay,
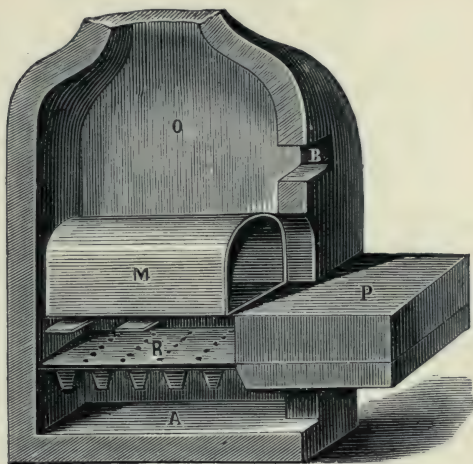
FIG. 29.

and introduced into the white-hot muffle, where it is left for a period corresponding to the colour desired. To save time, the plates may be pre-heated in a second muffle arranged above the first.

By this means a large range of tones can be obtained from one and the same material, by heating it to different temperatures; and the colours so produced are distinguished, not only by their warmth of tone, but also by very high stability. In fact, they may be

regarded as permanent, because very strongly calcined ferric oxide only passes very slowly into solution even under prolonged boiling in the strongest acids. Owing to this excellent property, which is equalled by very few other pigments, and the low cost of preparation, these colours deserve the most careful consideration by all manufacturers who are in a position to obtain suitable material in sufficient quantities.

(b) *Caput Mortuum, Colcothar*

Previous to the English method of making sulphuric acid by the oxidation of sulphur dioxide with nitric acid, this acid was manufactured by heating dehydrated ferrous sulphate (green vitriol); and even now, fuming sulphuric acid—oil of vitriol, or Nordhausen sulphuric acid—is largely obtained by the same process.

When anhydrous ferrous sulphate, $FeSO_4$, is exposed to a very high temperature—strong white heat—it is decomposed into sulphur trioxide, SO_3, sulphur dioxide, SO_2, and a residue, mainly composed of ferric oxide and a little basic ferric sulphate, which remains behind in the heating-pan. In fact, even at the highest possible temperatures obtainable in the furnaces used for the distillation of the green vitriol, it is impossible to recover the whole of the sulphuric acid, a small portion being tenaciously retained by the iron.

This red residue is sold under various names— colcothar, caput mortuum, English red, Indian red, etc.—and is used as a low-grade pigment, and also as a polishing agent. The name caput mortuum is a survival from the time of the alchemists, and was probably applied to indicate a dead-burned product, from which all the active ingredients had been removed.

Although, in former ages, this substance was held

in low estimation as a pigment, attempts have been made in recent times to convert it, by suitable treatment, into a more valuable product; and these attempts have been crowned with success, affording another instance of how a high commercial value can be imparted to a waste product by proper manipulation.

(c) Calcining Ferric Oxide

In order to obtain a series of tones of colcothar, it is subjected to repeated calcination, but not by itself, since it would require an extremely large quantity of fuel to effect any change of tone in view of the very high temperature the material has already been exposed to in the sulphuric acid plant. If, however, salt be added, then a variety of tones can be obtained without recourse to any particularly high temperature. It is frequently stated that the only effect of the presence of salt is to keep the calcining temperature uniform, inasmuch as the salt volatilises at a strong red heat, and when that temperature is reached, the whole mass cannot get any hotter until the whole of the salt has passed off, all the heat applied being consumed in transforming the salt into the state of vapour.

As a rule, however, the amount of salt added does not exceed 6% of the weight of the charge to be calcined; and this quantity does not seem to be sufficient to keep the temperature at a uniform level through the several hours required for the calcining process. The author is therefore of opinion that the salt also has a chemical action on the material during the calcination.

As already mentioned, colcothar is by no means pure ferric oxide, but always contains basic ferric

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sulphate.   Now, it is feasible that some reaction may take place between the basic sulphate and the sodium chloride at calcination temperature, with the formation of caustic soda, which, being a far more powerful base than ferric oxide, deprives the latter of sulphuric acid, sodium sulphate being formed.   The chlorine of the salt combines with the iron to form ferric chloride, which volatilises at a glowing heat.

According to this hypothesis, therefore, the addition of common salt in the calcination of colcothar is less for the purpose of maintaining a uniform temperature within certain limits than for decomposing the basic ferric sulphate present and inducing the formation of a product consisting entirely of pure ferric oxide. The various tones obtained are due to the varying length of exposure to the heat.

The following method is pursued in the conversion of colcothar into iron pigments on a manufacturing scale.   The crude colcothar from the sulphuric acid plant is ground, as finely as possible, in ordinary mills, and the resulting soft powder is intimately mixed with salt, 2, 4 or 6% being the usual proportions added. The calcination is ordinarily continued for six hours in the case of the mixture containing the largest amount of salt; but only two hours, or even one, for the other mixtures.

The operation is carried on in earthenware pipes, a large number of which (up to sixty) are built into a furnace.   The latter is fired very carefully, the temperature being raised only very gradually, since experience has shown that much better coloured products are obtained in this way than by raising the mass quickly to a high temperature.

When incandescent ferric oxide is allowed to cool

down with unrestricted access of air, the colour is not nearly so bright as when air is excluded during the cooling. Since air has no action on ferric oxide, this remarkable phenomenon cannot be due to the presence of the air, but probably to the influence exerted by the rapid change of temperature on the arrangement of the finest particles of the oxide. Nevertheless, some manufacturers hold that rapid cooling, with restricted access of air, improves the colour.

To exclude air from the ferric oxide during calcination, the open ends of the pipes are flanged and covered with close-fitting plates, which are luted with clay. The expansion of the internal air as it grows hot would burst the pipes unless a means of escape were provided, which consists in leaving small vent holes in the cover plates.

As previously mentioned, calcined ferric oxide is very inert, chemically, so that, when the calcination has been strong, prolonged boiling with the most powerful acids is needed to bring the oxide into solution. If the heating has been continued up to the strongest white heat, and the ferric oxide maintained in that condition for several hours, even hot sulphuric acid will have only a slight effect on the oxide, and the only way to make it more readily soluble is by fusion with potassium bisulphate.

Now indifference to chemical action is just the property required of a pigment for fine work; and in this respect, the ferric oxide colours are superior to all others. The gradations of tone that can be obtained from ferric oxide by varying the calcination are very numerous, comprising all between iron red, red-brown and pure violet.

The author has tried heating ferric oxide for a

considerable time at a very high temperature, equivalent to the strongest white heat, and obtained a product which was no longer pure violet, but had a decidedly blackish colour. Perhaps, by greatly prolonging the heating, it might be possible to get a pure black; but, even if this were so, the matter would be of no special interest, because black pigments for paints can be prepared in a much cheaper manner. All that would be accomplished would be the proof that ferric oxide actually undergoes an extensive molecular modification when heated.

FERRIC OXIDE PIGMENTS FROM ALUM SLUDGE

Alum is manufactured from alum shale and alum earth, the former being a carbonaceous clay shale interspersed with pyrites, and the latter a clay charged with pyrites and bitumen. The raw materials are left in heaps for several years, the pyrites being thereby oxidised with formation of free sulphuric acid and ferrous sulphate. This free acid reacts further on the clay, which it transforms into sulphate of alumina; and by leaching the heaps with water, a solution is obtained which contains the sulphate of alumina and the ferrous sulphate. On the liquor being concentrated, a basic ferric sulphate is deposited, which is worked up into red pigment.

For this purpose it is first levigated in a special manner, the sludge from the pans being placed in a large vat, suffused with water, and kept in slow circulation by stirrers, which distribute the particles in the water, forming a turbid liquid. This liquid is conducted into a gently sloping shute, the sides of which are perforated with openings at certain intervals, to

allow part of the liquid to run off into large collecting vessels underneath.

The heaviest of the suspended particles settle down first and are flushed out by the water escaping through the first opening. The finer the particles, the longer they remain in suspension, so that the liquid escaping through the last holes carries off only a very fine powder. The liquid collected in the different vessels is allowed to subside and is then drawn off from the
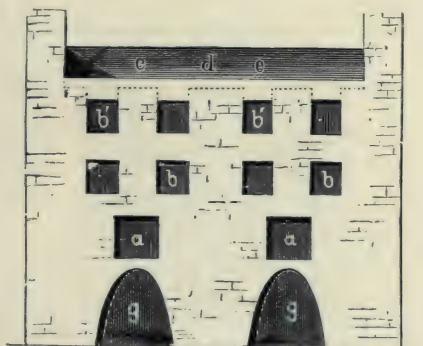
FIG. 30.

firm deposit. The operation is repeated with fresh quantities of sludge until sufficient sludge has been collected for further treatment. The collecting vessel furthest away from the intake of the shute contains the finest levigated material, and this is used for making the best ochres.

The levigated mass is dried in a very simple manner, being usually spread out on boards, which are exposed to the air in open sheds, covered with a roof to keep out the rain. Here the sludge is left until it forms a pasty or earthy mass, and is then calcined.

The best calcining furnace is of the type used for colcothar; but the pipes must be connected to an exhaust pipe for carrying off the vapours disengaged during calcination.

However, since alum manufacturers do not usually go in for making the highest-grade pigments, simpler calcining furnaces are used, consisting of reverberatory furnaces in which the heating-gases are allowed to act directly on the materials of the charge. A front
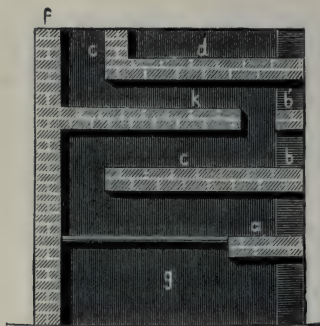
FIG. 31.

elevation and section of such a furnace are shown in Figs. 30 and 31. The furnace is constructed with several arches, one above another, marked c, k, d. The charge is introduced through the openings b and b'. The furnace chamber is at a, and the ashpit at g. The gases of combustion flow over the charge on the hearths of the several arches and escape, at the top, into the stack, along with the acid vapours liberated from the glowing mass.

The further the hot gases get away from the fire, the cooler they become, and therefore the less strongly heated the charge on the upper hearths. Consequently,

the resulting product (ferric oxide) from the different stages of the furnace differs in colour; and a number of gradations can be obtained by blending. The ferric oxide pigments prepared in this way are not pure oxide, but also contain small quantities of sulphuric acid and metallic oxides which were present in the original crude sludge. However, by reason of the simple process of preparation employed, these pigments are usually sold at lower prices than those from colcothar; and for less fine work they are excellent.

CHAPTER VII

BROWN EARTH COLOURS

In point of chemical composition, the majority of the brown earth colours are closely allied to the reds, both kinds containing ferric oxide. The main difference consists in that, in the brown earths, the ferric oxide is combined with water to form ferric hydroxide.

Many of the brown earth colours, however, are of entirely different chemical composition. and either consist mainly of organic matter derived from the decomposition of plants—and therefore very similar to brown-coal or peat—or else contain varying quantities of inorganic substances mixed with these dark-coloured organic decomposition products.

The brown earth colours form a highly important group, some of the members of which are used in the finest paintings, and, for certain purposes, cannot be replaced by other pigments. Those containing ferric hydroxide are found—though not very frequently—in natural deposits, the most celebrated being the terra di Siena, occurring in the vicinity of that city.

TERRA DI SIENA

This highly renowned pigmentary earth is found in deposits, and, in the crude state, forms dark brown masses which are devoid of lustre, crumble readily between the fingers, have a smooth conchoidal fracture

and absorb water with avidity, in consequence of which property they adhere to the tongue. Their chief chemical constituent is ferric hydroxide, with which, however, variable quantities of sand, clay and ferric oxide are admixed. These admixtures cause a considerable divergence in the colour of the earth, ranging from pure brown to reddish-brown, and, in the case of very impure lumps, to an unsightly yellow-brown.

Mineralogically, terra di Siena is often regarded as a distinct species which, according to the results of analysis, must be considered, not as ferric hydroxide, but as ferric silicate combined with water. Sometimes, a portion of the ferric oxide is replaced by alumina, so that the percentage composition of the mineral becomes approximately: ferric oxide, 66%; silica, 11%; alumina, 10%; and water, 13%. The hardness of this mineral is $2\cdot5$, and the sp. gr. $3\cdot46$.

The method of formation of terra di Siena was probably on the same lines as that already described in the case of ochre, namely by the breaking down of minerals—in this case brown ironstone—and natural levigation, the powder being deposited in places where the water containing the ferric hydroxide in suspension came to rest and allowed the solid particles to settle down.

The best lumps of terra di Siena in point of purity and colour can be used as pigments without any preparation; but in most cases the earth is lightly calcined, in order to improve the colour. This treatment enables a whole series of tones, from pure brown to the brightest red, to be obtained. The stronger the heating, the more water expelled from the hydroxide, and consequently the closer the approximation of the colour to that of ferric oxide.

The pigments met with in commerce as terra di Siena can also be prepared artificially, by making ferric hydroxide and heating this, when dried, until the requisite tone is attained. For this purpose, ferrous oxide is precipitated from green vitriol and exposed to the air, under which conditions it is rapidly transformed into ferric oxide, and the greyish-green colour of the mass changes to brown. Lighter tones can be obtained by the addition of inert white substances; and, in other respects, the method of preparation is the same as that of artificial ochre.

These pigments are sold under various names, the dark shades, between pure brown and red brown, being usually called terra di Siena or mahogany brown, whilst the paler sorts are sold as satinober—more correctly satin ochre, golden ochre, etc. Other pigments, chemically allied to the ferric oxide or ochre pigments, are sometimes found on the market under various and entirely arbitrary names.

It may be pointed out that the greatest confusion exists in the nomenclature of pigments, to such an extent that, in many cases, neither the chemist nor the manufacturer knows precisely what pigment is implied by a given name. The confusion is still further increased by the use of names taken from different languages.

True Umber

Umber, properly so called—also known as Turkish, Cyprian or Sicilian umber, from the country of origin—derives its name, according to some authorities, from the province of Umbria (Italy), where a brown earth is found, though others ascribe it to the Latin " umbra "

(shade) because of the pigment being used for painting shadows.

True umber is an earthy mass of fine texture and liver-brown colour, merging into chestnut in some of the lumps. Chemically, it consists of a double silicate of iron and manganese combined with water, a portion of these metals being usually replaced by alumina. The greater hardness (1·5) and higher specific gravity (2·2) of true umber in comparison with Cologne earth (which is quite arbitrarily termed " umber "), form a ready means of differentiation between the two.

According to Viktor Merz, the umber found in Cyprus consists of : ferric oxide, 52%; manganese oxide, 14·5%; and alumina, 3%; and is, possibly, merely a mixture of clay with hydroxide of iron or manganese. An umber examined by Klaproth contained 13% of silica, 5% of alumina, 48% of ferric oxide, 20% of manganese oxide and 14% of water.

The tone of umber can be modified, in the direction of red, by calcination, but this process is seldom employed, the dark brown shade of this colour being the one most appreciated.

In some parts of northern Germany, Thuringia in particular, the iron mines contain smaller or larger pockets of ferric hydroxide, of a fine earthy texture, from which umber is prepared, by levigation and calcination. The product is sold under various names : chestnut brown, wood brown, mahogany brown, bistre flea brown, roe brown, according to the shade of the calcined pigment.

A mineral (" siderosilicate," according to Von Walterhausen) composed of ferric silicate, and approximating in this respect to terra di Siena, is found in the neighbourhood of Passaro (Sicily) in deposits of tuff. It forms

masses which are transparent at the edges and are usually liver-brown to chestnut in colour. The hardness of the mineral is 2·5, the sp. gr. 2·713, and the average chemical composition : silica, 34% ; ferric oxide, 48·5% ; alumina, 7·5% ; and water, 10%.

The foregoing are only a few examples of brown or red-brown earth colours. In all these minerals the pigmentary principle is iron, in combination either with oxygen alone (ferric oxide), with oxygen and water (ferric hydroxide), or silica compounds (ferric silicate), and always associated with certain quantities of other metallic oxides, especially alumina and manganese oxide. Although but few of these minerals have gained any special reputation as pigments, there is no doubt that similar minerals, which are certain to occur in or near many deposits of iron ores, could equally well be used for that purpose. There is no need to emphasise that the discovery of such a mineral would be a very valuable find, and that the products obtainable therefrom could be utilised to great advantage.

The testing of a mineral for its suitability as pigment is a very simple matter, all that is required being to subject a small quantity to the same treatment that is applied to the earth colours on a large scale. For this purpose a few pounds of the mineral are levigated, and the residue is dried. To ascertain the tones obtainable by calcination, small samples—of about 100 grms.—are placed in crucibles, and gradually heated in a furnace. When the masses have attained a sufficient temperature, the samples are taken out of the furnace, at intervals of ten minutes, and left to cool. It will then not be difficult to decide whether the mineral is at all suitable for the purposes of the

colour-maker; and if so, these tests afford at once an indication of the temperature and time the mineral must be heated in order to obtain pigments of definite tones.

COLOGNE EARTH (COLOGNE UMBER)

The application of the term "umber" to this earth can only have been based on a certain similarity in colour to true umber. In chemical composition, however, the two are quite different, Cologne earth really consisting of a mixture of humic substances. It is well known that the rotted wood found in the interior of decaying trees is often a handsome brown colour; and all woody matter, after lying a very long time, finally acquires this colour, owing to the transformation of the wood into dark-coloured compounds richer in carbon. This effect can be seen on the large scale, in Nature, in the case of coal, brown coal and peat.

Now Cologne earth consists of a brown-coal mould, dark brown in colour, of earthy character and of such low cohesive power that it crumbles with ease. Owing to this character, Cologne earth can be easily ignited by the flame of a candle, and then burns with a strong, smoky flame, leaving very little ash and disseminating the peculiar bituminous smell given off when brown coal is burned.

The geological characteristics of Cologne earth enable one to conclude that, where similar conditions prevail, materials of analogous nature may be discovered. This earth is found embedded in a deposit of brown coal, in which it forms pockets, and occasionally large bodies. Now, brown-coal deposits of enormous extent occur in very many localities, as for instance in Upper Austria

and in Bohemia; and many of these mines are sure to contain pockets of brown-coal mould, which have perhaps been overlooked, but might very well be utilised in the preparation of colours of very similar character to Cologne earth.

The preparation of this material is very simple. The earth coming from the deposits is put through a simple levigation treatment which leaves, as residue, lumps of semi-decomposed wood, mineral admixtures, sand, etc. The levigated earth is sold in the form of cubes.

Cologne earth comes into the market under various other names, such as : umber, Cassel brown, Spanish brown, etc.

The fiery brown which was so greatly preferred by the famous painter Van Dyck, and named Vandyke brown after him, was of very similar composition to Cologne earth, and is said to have been obtained from a deep brown peat earth. The Vandyke brown of the present day, however, is almost invariably a ferric oxide pigment, toned to the proper shade by suitable calcination.

Asphaltum Brown (Bitumen)

As a natural product, which can be used as a painters' colour without any special preparation, asphaltum (bistre, bitumen) may also be classed among the earth colours. Chemically, it is composed of hydrocarbons of various kinds, and is thus similar to tar; in fact, asphaltum may also be regarded as a natural tar resulting from the decomposition of various organic substances. Many deposits of this mineral are known, and two of them are particularly celebrated : those

of the Dead Sea, in Syria, and the Lake of Asphalt, in Trinidad. Both deposits consist of craters filled with water on which the asphaltum floats in large cakes.

Several kinds of asphaltum are met with in commerce, ranging in colour from brown to black. The preparation of the material as a pigment is confined to grinding the mass, which is always of a low degree of hardness. Being readily soluble in oil of turpentine and then furnishing the most beautiful brown tones when laid on thinly, the pigment is usually sold in this condition, although it is also ground in oil for the same purpose.

Finally, it may be mentioned that various useless materials can be transformed, by suitable treatment, into brown pigments closely resembling Cologne earth and applicable to the same uses. Such pigments can be prepared from brown-coal slack (from inferior brown coal) or bituminised wood—a variety of brown coal looking like charred wood—by treating these materials with a lye made from wood ashes and lime, and washing and drying the residue.

CHAPTER VIII

GREEN EARTH COLOURS

ALTHOUGH the number of green-coloured minerals is large, but few of them are suitable for painters' colours, because they occur so rarely in Nature that their employment for this purpose is out of the question, more especially since a very large number of green pigments can be obtained by artificial means. The most important of the earth colours in this category are Celadon green, or green earth, and malachite green —the latter, however, less so, because the substance of which it is composed can be prepared artificially.

GREEN EARTH, OR CELADON GREEN

This mineral is of a peculiar green colour, and the name " Celadon green " has been universally adopted in the nomenclature of colour shades. Green earth occurs native in many places, being the decomposition product of an extensively distributed mineral, augite, crystals of which are found in many of the deposits. The green earth of Monte Valdo, on Lake Garda (Upper Italy) has been used for a very long time as a pigment. It is chiefly prepared in Verona for distribution in commerce, and from this circumstance has acquired the name " Verona green," or " Verona earth." The earth is also found in Cyprus and Bohemia, where it

frequently occurs as the decomposition product of basaltic tuff. However, whether obtained from Monte Valdo or elsewhere, the product is always placed on the market as Verona earth.

Native green earth is always tough, mostly occurring in amygdalous lumps, but occasionally in the crystalline form of augite. It has a fine-grained fracture, a hardness between 1 and 2, and a sp. gr. between 2·8 and 2·9. The colour is not always quite uniform, pure lumps having the characteristic Celadon green appearance, whilst impure lumps are olive green to blackish green. In chemical composition it is chiefly ferrous silicate, and this compound must be regarded as the actual pigmentary principle of green earth. In addition, it contains varying quantities of other compounds which influence the depth of shade of the product.

Verona earth chiefly consists of ferrous oxide in combination with silica; alumina, magnesia, potash, soda and water being also present. Analysis shows it to contain: ferrous oxide, 21%; silica, 51%; magnesia, 6%; potash, 6%; soda, 2%; and water, 7%.

The green earths from Gösen, Atschau and Männelsdorf, near Kaaden (Bohemia) and the Giant's Causeway (Ireland) have the following composition:

	Kaaden.	Giant's Causeway.
Silica	41	56·4
Alumina	3	2·1
Ferrous oxide	23	5·1
Ferric oxide	—	14·1
Lime	8	—
Magnesia	2	5·9
Potash	3	8·8
Carbon dioxide	19	—
Water	—	6·8%

On account of the large quantity of mechanically associated water, freshly dug green earth is greasy in character, like wet clay. In partial drying, most of this water evaporates, the mass becoming earthy and adherent to the tongue. Sometimes the colour is an ugly brownish-green, owing to the presence of a considerable amount of ferric oxide formed as the result of changes set up by exposing the mineral to the air. Ferrous oxide is a very unstable compound, having an energetic tendency to combine with more oxygen and thus undergo transformation into ferric oxide; so that when green earth is left in the air for a long time, a considerable proportion of its ferrous oxide is oxidised to ferric oxide, the mass thereby assuming the brown tone in question.

Such an unsightly product can, however, be converted, by simple treatment, into one of very bright and handsome appearance; and it is this possibility that first enabled green earth to attain importance as a painters' colour. Formerly it was only used as a material for common work, being added to whitewash or employed for indoor paints.

When the crude green earth is treated with very diluted hydrochloric acid, the compound of ferrous oxide and silica is left intact, but most of the extraneous admixtures are removed. Ferric oxide, in particular, passes into solution, and the calcium carbonate largely present in some kinds of green earth is also dissolved. After prolonged contact with the crude earth, the acid liquor takes on a brownish coloration from the dissolved ferric oxide. Since the presence of iron salts has no influence on the purification of the green earth, the most impure, highly ferruginous hydrochloric acid can be used, and the liquor can afterwards be

employed in the preparation of artificial ochre by leaving it in prolonged contact with any strongly ferruginous mineral, such as brown ironstone, which neutralises the surplus acid. This liquor is then precipitated by lime, alkali, etc., the resulting deposit consisting mainly of ferric hydroxide, the further treatment of which is conducted exactly as described in dealing with the preparation of artificial ochre.

The treatment of the crude earth is best carried on in the same vessels as are to be used in the subsequent levigation process. After the acid liquor has been drawn off, the earth is brought into contact with water, stirred up well, and the water run off, by opening tap-holes in the side of the vessel, into settling-tanks, where it is left until all the suspended matter has completely subsided.

The colour of green earth can also be toned by the addition of yellow ochre, thus producing a range of greens with a yellowish tinge. These lighter shades, however, are seldom met with in commerce, the trade judging the quality of green earth more particularly on the depth of colour.

Green earth is a valuable pigment for all kinds of painting, on account of its extreme permanence. It may be applied directly over lime without suffering any change, whereas most of the cheap green colours are destroyed in like circumstances. This behaviour renders green earth specially valuable in fresco work, although it is also largely used as an oil colour.

Augite is of frequent occurrence in volcanic districts; and in such localities, deposits of green earth are certain to be found. The test for the suitability of a green earth consists mainly in treatment with dilute hydrochloric acid. If the mineral assumes a handsome green

tone, it will generally form a useful pigment. The test may be supplemented by applying the colour to a fresh coating of whitewash, under which conditions it should remain unaltered.

Artificial Green Earth (Green Ochre)

A product sometimes put on the market as green earth or green ochre has nothing beyond its name in common with green earth properly so called, except a certain similarity in colour. This pigment is prepared by mixing yellow ochre to a thin pulp with water and adding about 2% (of the weight of ochre) of hydrochloric acid. After a few days, a solution of 2 parts of yellow prussiate of potash is added, and if the liquor still gives a precipitate when tested with ferrous sulphate, this last-named salt is added so long as such a precipitate continues to form.

The deposit is washed, and dried in the ordinary way. When the right proportions have been taken, a pigment is obtained that coincides fairly in point of tone with true Verona earth. It is, however, inferior in point of permanence, the Berlin blue present being somewhat unstable and decomposing very quickly when brought into contact with lime. The reaction taking place in the production of so-called " artificial Celadon green " is that the hydrochloric acid used dissolves ferric oxide from the ochre, the addition of the yellow prussiate of potash then forming a blue precipitate of Berlin (Paris) blue which, in conjunction with the yellow of the ochre, gives a green-coloured mixture.

MALACHITE GREEN

Although the pigment sold under this name is nearly always an artificial product, it cannot be omitted from a work dealing with the earth colours, because, in former times, it was prepared exclusively from the mineral malachite. Owing to the fact that artificial malachite green is one of the cheapest of colours, the troublesome work involved in the mechanical preparation of the native pigment has been almost entirely abandoned, and the malachite itself is now utilised to greater advantage as a source of copper.

Malachite green (or mountain green) is found in nearly every case where copper ores exist, and is still—though very rarely indeed—prepared, in a few places, from the mineral, the dark-coloured lumps being picked out because the lighter-coloured ones would furnish much too pale a colour.

The treatment of malachite for the preparation of pigment presents certain difficulties owing to the comparative hardness (3·5–4) of the mineral, which is also rather heavy (sp. gr. 3·6–4·0). On the large scale, the selected mineral is first put through a stamping-mill, and then ground, very hard stones being required for this purpose. The fine product from this (usually wet) process is levigated and dried.

The pit water of some copper mines contains certain quantities of blue vitriol (copper sulphate) in solution; and such pit water is generally treated for the recovery of a very pure form of copper, the so-called cementation copper. The liquor might also be worked up into malachite green, by collecting it in large tanks and precipitating the dissolved copper oxide with milk of lime, the bluish-green deposit separating in association

with gypsum being transformed into a light malachite green by washing and drying. A darker green, free from gypsum, could be prepared by using a solution of carbonate of soda as precipitant.

Neither the native nor the artificial malachite green is particularly handsome in colour; and both possess, in addition, the unpleasant property of gradually going off colour in the air, all the copper compounds being quite as sensitive to sulphuretted hydrogen as those of lead, and finally turning quite black under the influence of that gas.

CHAPTER IX

BLUE EARTH COLOURS

ONLY three minerals are known to be suitable as pigments; and indeed, at present, only two, the third, lapis lazuli, being now of merely historical interest. Nowadays, no one would think of using this rare and expensive mineral as a pigment, since ultramarine, which has the same pigmentary properties, is extremely cheap, whereas the pigment from lapis lazuli was worth its weight in gold. The only two blue earth colours of any interest at present are malachite (copper) blue, and the blue iron earth Vivianite; and even these, though by no means rare, are little used, since artificial blues are now made which are far superior in beauty and can be obtained so cheaply that the natural pigments are put out of competition.

MALACHITE BLUE (LAZULITE)

Lazulite and malachite (mountain blue) are of frequent occurrence in copper mines, and the former is distinguished by its beautiful azure blue colour, which, however, suffers considerably when the crystals are reduced to powder. Both minerals are very similar in chemical composition, and consist of cupric carbonate. The formula of malachite is $2CuOCO_2 + H O$, that of lazulite being $3CuO(CO_2)_2 + H_2O$, so that

the only difference between them is that of the relative proportions of the substances in combination. Lazulite is also rather hard (3·5–4·0), but owing to the small size and brittle character of the crystals it is not very difficult to pulverise. In the air, malachite blue behaves in much the same way as malachite green, turning black in presence of sulphuretted hydrogen.

Malachite blue is chiefly used for indoor work, and also as a water colour; but it is always rather pale and dull.

Vivianite

This mineral—also termed blue ochre—is a transformation product of various iron ores, and occurs native as fairly extensive deposits in some places, especially in peat bogs. It forms ill-defined crystals, which are of a low degree of hardness (2·0) and vary in specific gravity between 2·6 and 2·7. The colour of the freshly won mineral is whitish or pale blue, but soon changes to a dark blue in the air, owing to the oxidation of the ferrous phosphate, originally present, into ferric phosphate.

Vivianite can be transformed into a pigment by a simple process of crushing and levigation; but the product is never very handsome, and, at best, is only suitable for quite common paint work, though characterised by considerable stability.

CHAPTER X

BLACK EARTH COLOURS

ONLY two minerals are known that can be used as black earth colours, namely black chalk or shale black, and blacklead or graphite. Whereas the former of these is of merely subordinate importance, most of the black chalks being prepared artificially, graphite is all the more so because it is employed, not only as the sole material for lead pencils, but also for making graphite crucibles, as blacklead stove polish, as a lubricant, etc. One of its numerous applications is in connection with the electro deposition of metals, its high electrical conductivity causing it to be used for coating the interior of the moulds in which this deposition is effected.

GRAPHITE

Graphite, also known as plumbago or blacklead, consists of carbon. It is usually spoken of as pure carbon, but from a very large number of carefully conducted analyses, it would appear that native graphite is never quite pure, even the finest grades of the mineral containing 96·8% of carbon at the most. The accompanying substances—which in some cases

form nearly 50% of the whole—are of divergent com-
position and consist of iron, silica, lime, magnesia and
alkalis. Even the combustible constituent of graphite
is not pure carbon, but always contains a certain—
though small—proportion of volatile substances. These
slight traces of volatile matter are of considerable
importance in connection with the hypothesis on the
origin of the mineral.

Contrary to the old idea, it is now almost universally
considered that, instead of being of volcanic origin,
graphite consists of the remains of long-dead organisms,
and in this respect is closely related to coal. This
hypothesis, however, fails to explain one point, namely
the crystalline nature of graphite; for even anthracites,
which form the oldest coals known to have had their
origin in the decomposition of organic substances, do
not reveal the faintest traces of crystalline structure.
The upholders of the theory that graphite was formed
by the action of plutonic forces adduce, in support,
the fact that graphite can actually be produced, in
certain chemical processes, at high temperature.
Molten cast-iron in cooling causes the separation of
carbon in the form of graphite; and the same substance
is also formed, in large quantities, in gas retorts,
through the decomposition of certain carbonaceous
compounds when brought into contact with the
glowing walls of the retorts. Recent investigations,
however, have shown that the temperature necessary
for the transformation of non-crystalline carbon into
crystalline graphite is by no means so high as was
formerly supposed; and it is now known that the change
takes place at as low as red heat. Possibly the two
theories could be reconciled by the assumption of a
very old coal—such as is found, for instance, as anthra-

cite in many parts of the world—being so strongly heated, by plutonic action, as to change into graphite.

Native graphite crystallises in the form of hexagons, mostly tabular; but really well-developed crystals are of extremely rare occurrence, and by far the greatest quantities of this mineral are found in the condition of dense lumps, in which only the crystalline structure, and not any decided crystals, can be discerned. The hardness of the mineral fluctuates within fairly wide limits, ranging from 0·5 to 1·0. The sp. gr. averages 1·8018–1·844, but, in the case of impure lumps may increase to 1·9–2·2.

The following analyses will give some idea of the considerable divergence existing between graphites from different deposits :—

SIBERIAN GRAPHITE

						1	2
Carbon	.	.	.	.	.	94·28	40·55
Ash .	.	.	.	.	.	5·72	56·56
Water	.	.	.	.	.	—	2·80

PORTUGUESE GRAPHITE

Carbon	.	.	.	.	.	.	42·69
Water (chemically combined)				.	.	.	3·96
Ash .	.	.	.	.	.	.	53·35

BOHEMIAN GRAPHITE

						1	2
Carbon	.	.	.	.	.	61·01	69·04
Alumina	.	.	.	.	.	7·80	6·86
Silica	.	.	.	.	.	17·34	14·18
Magnesia	.	.	.	.	.	1·03	0·53
Lime .	.	.	.	.	.	2·56	0·80
Ferric oxide	.	.	.	.	.	5·54	4·00
Potash	.	.	.	.	.	0·87	0·91
Water and volatiles	.	.	.	.	.	3·24	2·89
Sulphur	.	.	.	.	.	0·51	0·62

GRAPHITES FROM UPPER STYRIA

	1	2	3
Carbon	85·00	87·16	82·21
Ash	14·89	12·66	17·92

	4	5	6
Carbon	82·40	81·10	55·50
Silica	12·38	11·61	21·00
Alumina	3·90	5·60	14·56
Ferric oxide . . .	0·53		
Manganese protoperoxide .	0·62 ⎫	2·00	4·84
Lime	0·02 ⎬		
Alkalis	Trace	Trace	0·62
Sulphur	—	—	0·30
Loss on incineration . .	—	—	2·43

Of these Styrian specimens, Nos. 1-4 are crude kinds, of sp. gr. 2·1443; No. 5 was levigated in the laboratory, and No. 6 was levigated from an inferior quality at the mine.

According to the character of the crystalline structure, the colour of graphite varies, but is mostly deep black. Very pure specimens, such as the beautiful graphite blocks (from the renowned Alibert graphite mines in Siberia) which, as a rule, are only to be seen in exhibitions and mineralogical collections, have the appearance of unpolished steel or white pig iron (spiegeleisen). The most important property of native graphite is its low hardness and cohesion, in consequence of which it leaves a streak when drawn over the surface of paper.

Graphite seems to be of frequent occurrence all over the world, though only few deposits are known which yield a product that is suitable for all the purposes to which graphite is applied.

In European countries, Austria is particularly rich in graphite; and very large deposits of this mineral are found in Bohemia. Considerable deposits also occur in Bavaria, where they have long been worked.

English graphite is celebrated for its excellent quality. All these European deposits, however, are surpassed, both in extent and in the quality of their products, by those discovered in Siberia, the largest being that producing the aforesaid Alibert graphite and situated, near the Chinese frontier, in eastern Siberia. At one time, America imported all her blacklead pencils from Europe, having, at that period, no known graphite deposits furnishing a suitable product. At present, however, deposits of this kind have been found in California, and there can be little doubt but that many others of this valuable mineral remain to be discovered in that enormous continent, the geological investigation of which is still far from being complete.

The graphite of some deposits is so highly contaminated by extraneous minerals that it cannot be utilised, since the cost of purification would exceed the value of the product. On the other hand, the purer kinds, when suitably refined, yield a graphite that is fully adapted to all requirements.

The refining process may be either chemical or mechanical, the choice of methods depending entirely on the character of the associated minerals. If these mainly consist of coarse, stony fragments, preference should be given to mechanical treatment; but if they are of such a character that they cannot be eliminated in this way, chemical methods must be employed. Sometimes the two systems are combined, by first subjecting the graphite to a rough mechanical purification, and then completing the operation with chemical reagents.

The mechanical treatment consists in first removing as many of the impurities as possible by hand-picking, and grinding the remainder in edge-runner mills, along

with water. The turbid liquid, containing the powdered graphite and extraneous minerals in suspension, is led through long launders, the sides of which are notched at intervals to allow the water to overflow into large pits. The graphite settling in the first of these pits contains numerous particles of the heavy associated minerals; but that remaining suspended in the water and carried on to the further pits constitutes the bulk. The water is left to clarify completely in the pits, and is then drawn off, the pasty residue being shaped into prisms, which are compressed under heavy pressure, to increase their density, when partially dry.

Although levigation will remove most of the accompanying extraneous minerals, it cannot eliminate the ash constituents of the graphite. Experiments made in this direction have demonstrated that the ash content of the levigated graphite is exactly the same as that of the crude material. Whilst these ash constituents do not affect the quality of graphite for certain of its uses, they nevertheless impair its beautiful black colour to a considerable degree. The chemical treatment necessary to eliminate these constituents is attended with many difficulties, the chief of which resides in the fact that the ferric oxide present is in a form that is not readily accessible to the action of chemicals. For this reason, attempts to purify graphite with crude hydrochloric acid are hardly likely to prove successful, since both the ferric oxide and the accompanying silicates obstinately resist the action of this acid.

In order to obtain graphite of a high state of purity, the attempt must be made to bring this ferric oxide and the silicates into a soluble condition. This can be accomplished in various ways, and the choice of

the method will depend on the purpose for which the graphite is intended. For example, the operations may either be confined to purification, or else include the attainment of a maximum condition of subdivision. When foliaceous graphite has to be treated—and this kind of graphite cannot, in its original condition, be used for making lead pencils—it is preferable to employ a method which will produce both the above results. The purification may consist in crushing the graphite to powder, and fusing this with a mixture of sulphur and carbonate of soda, whereby the silicates present are converted into soluble compounds, and the ferric oxide into ferric sulphide. On extracting the melt with water, a portion of the contained salts pass into solution and is carried off. The residue is then treated with dilute hydrochloric acid, which dissolves out the ferric sulphide, with liberation of sulphuretted hydrogen, and leaves the graphite in a very pure condition after washing.

In order to render foliaceous graphite suitable for lead pencils, a different method is pursued, but should only be employed in special circumstances, on account of the expense entailed.

According to the process recommended by Brodie, the graphite, ground to coarse powder, is mixed with about one-fourteenth of its own weight of chlorate of potash, this mixture being heated, with two parts by weight of sulphuric to each part of graphite, in a water bath so long as fumes of hypochlorous acid continue to be disengaged. The heating must be performed in stoneware or porcelain vessels, those made of any other materials being strongly corroded by the chlorine compounds formed.

When the evolution of fumes ceases, the mass is

allowed to cool, and is carefully washed with a large volume of water, the residue being then dried and heated to redness.   During this calcination the graphite under-goes a peculiar change, increasing considerably in bulk and forming an exceedingly soft powder which, after another washing, consists almost entirely of chemically pure carbon.

Graphite purified in this way can be used for any purpose for which this material is employed, and may be made into the finest lead pencils.   However, as already mentioned, this process is usually too expensive for general application.

The use of graphite for writing is more ancient than is usually supposed, having been tentatively employed between 1540 and 1560.   It was during this period that the graphite mines in Cumberland were discovered ; and the extremely pure graphite found there soon began to be used as a writing material.

Up to the close of the eighteenth century, lead pencils were made by selecting pure lumps of graphite and sawing them into thin rods, which were then encased in wooden sticks.   Apart from their high price, these pencils exhibited various defects, one of the chief being that a stick of such pencil was seldom of uniform hard-ness throughout its length, most of them being so soft in parts as to make a deep black, smeary mark, whilst other parts would hardly give any mark at all.

The defects inherent in native graphite are com-pletely removed by the method now generally employed in making lead pencils ; and on this account the old process of sawing the lumps has been abandoned.

Graphite with a fine earthy texture alone is suitable for lead pencils, scaly varieties being useless for this purpose, unless specially prepared, since they will not

give a solid black streak. By means of the Brodie process, however, even the most highly crystalline kinds can be rendered suitable for this purpose. Siberian graphite is distinguished by extremely high covering power, and is specially preferred for the manufacture of pencils. Excellent varieties for this purpose are also found in many parts of Europe; and indeed, a large proportion of all the lead pencils used throughout the world are made from Bohemian, Styrian and Bavarian graphite.

At present, all pencils are made from ground graphite, the extremely finely ground and levigated material being kneaded into a paste with clay. This operation fulfils a twofold purpose, the plasticity of the clay increasing the cohesion of the individual particles of graphite, whilst the amount of clay used determines the hardness of the pencil.

The larger the proportion of clay, the harder the pencil when baked, and therefore the paler the mark the pencil will make on paper. In the pencil factories, the clay is incorporated in special machines; and the operation requires extreme care, since only a perfectly uniform mixture will give a composition of regular character in all cases.

The intimately mixed material is formed into thin rods, which are dried and then baked, the heat driving out the water in the clay and transforming it into a solid mass.

An addition to this main application of graphite, the mineral is also used for making crucibles, chiefly for melting the noble metals. Crucibles of this kind are largely manufactured near Passau, Bavaria, and similar crucibles are made in England from Ceylon graphite.

Another important use for graphite is as a coating for iron articles to protect them from rust. For this purpose, however, only the inferior kinds are employed; and these can also be made up into excellent cements capable, in particular, of offering considerable resistance to the action of heat and chemicals.

To complete the tale of the applications of graphite, its employment as a lubricating agent for machinery, especially for reducing friction in machines made of wood, may be mentioned. Latterly also, the finest levigated graphite has come into use, in admixture with solid fats or mineral oils, for lubricating large engines, for which purpose it is excellently adapted.

BLACK CHALK

Black chalk, slate black, Spanish chalk, crayon, etc., is not a chalk at all, in the mineralogical sense, but consists of clay shale of varying colour. Some kinds of this shale are pure black, almost velvet black, and these are considered the best. Others have a more greyish or bluish tinge and are of low value as pigments.

The purer the black, the finer the grain of the material, and therefore the greater its value to the colour-maker. The variety obtained from Spain is generally admitted to be the best, and for this reason the name of Spanish chalk has been applied to all similar minerals.

In all cases the black colour of Spanish chalk is due to carbon; but the particular modification of carbon present has not yet been accurately identified. According to some, it is chiefly graphite, whereas others ascribe the colour to amorphous carbon. Apparently, the

material found in different deposits contains either one or the other of these modifications of carbon.

Deposits of black chalk are fairly plentiful, but in many of them the material is so contaminated with extraneous minerals that a somewhat troublesome method of preparation is needed to fit them for the purpose of the draughtsman. With this object, the native product must be ground extremely fine, and the powder levigated; and owing to the expense of these processes, they are now seldom used, it being possible to obtain a good black chalk far more cheaply than by levigating the natural material.

This artificial black chalk is prepared by mixing ordinary white chalk, or white clay, with a black colouring matter, shaping the mass into prisms, and sawing these into suitable pieces when dry. The white pigment may either be mixed with some very deep black substance, such as lampblack, or stained with an organic dyestuff, which is, in reality, not black, but either very dark blue or green.

The usual colouring matter used with white chalk is lampblack, mixed to a uniform paste with thin glue, a suitable amount of clay or chalk being incorporated with the mass. The production of a perfectly homogeneous mixture entails subjecting the paste to a somewhat protracted mechanical treatment. When the mass has become perfectly uniform throughout, it is shaped into prisms, which are exposed to the air to dry and are then cut up with a saw. Instead of prisms, the mass can be shaped into thin sticks, which dry more quickly.

A very handsome black chalk can be made, with comparatively little trouble, by treating chalk with a suitable quantity of logwood decoction previously

mixed with sufficient green vitriol solution to render the liquid a deep black. This liquid is added to the dry chalk, intimately mixed therewith, and the pasty mass shaped into sticks. The colouring agent may be replaced by a solution of logwood extract blackened by the addition of a small quantity of chromate of potash; or black dyestuffs may be used.

CHAPTER XI

MENTION has already been made of the great confusion prevailing in the nomenclature of pigments, and that many of these are put on the market under a variety of names taken from different languages.

Although the number of the earth colours is far smaller than that of the artificial colouring matters, the nomenclature is in a no less confused condition.

Most frequently, earth colours are named after the localities where they are either discovered or prepared, in combination with the word indicating the colour of the product—for example : Cologne white, Vienna white—or the term " earth " (Verona earth, Veronese green, etc.). Whilst these names give, to some extent, an indication of the nature of the pigment, others have no reference to it at all; such as colcothar, bole, umber, etc. Finally, a number of other names in use are calculated to produce the impression that the earth colours in question are of an entirely different nature to their real one. As an example, we may cite the name " French chalk," which is not a chalk at all, but consists of the mineral talc. Black chalk, again, is not chalk (calcium carbonate), but a black shale; and graphite is often termed blacklead, although it contains no lead at all, and the name is

merely a survival from the time when pencils of metallic lead were used for drawing.

In order to bring some kind of order into the various names which are applied to the earth colours, a list of those in current use is appended. Many of these names, it may be stated, have been selected in a purely arbitrary manner, some manufacturers, for instance, selling ordinary chalk under a variety of foreign names, for the purpose of thereby obtaining higher prices. These borrowed names would seem to be superfluous, to say the least. Pure and properly levigated chalk is the same article everywhere, whether prepared from English, French or German limestone; and in all cases the simple name, " chalk," with an explanatory " single," " double," or " triple " levigated, should be quite sufficient.

In the case of earth colours that are really obtained of special quality in certain localities, such as terra di Siena, green earth from Verona, or the like, the corresponding name might be retained, even if the pigment did not originate from the locality in question, as a generic term for a pigment possessing certain properties and of a certain composition.

In the following classification, the names of the earth colours are given in accordance with their colour and chemical composition.

White Earth Colours

Carbonate of Lime :
Chalk; levigated chalk; Vienna white; Spanish white; marble white; artists' white; Bougival white; Champagne chalk; Paris chalk; Cologne chalk; Mountain chalk; craie; blanc minéral; Blanc de

Champagne; Blanc de Meudon; Blanc de Bougival; Blanc de Troyes; Blanc d'Orleans; Blanc de Rouen; Blanc de Briançon.

Basic Carbonate of Lime :

Vienna white; Vienna lime; pearl white; whiting; Blanc de chaux; Blanc de Vienne.

Note.—The calcareous marls, consisting of carbonate of lime and clay, are also frequently sold under the above names, the same being the case with gypsum.

Silicate of Alumina :

White earth; pipeclay; Dutch white; Cologne earth; terre d'Argile; Argile blanc; Terre blanche.

Silicate of Magnesia (mineralogically, talc and soapstone) :

Talc; Venetian earth; French chalk; Venetian white; glossy white; feather white; shale white; face-powder white; Blanc de Venise, Blanc d'Espagne; Blanc de fard.

Note.—Fine grades of white lead are also sold as Venetian white, Spanish white and shale white; but can easily be recognised by their weight. The term " prepared " white, frequently applied to earth colours in the trade, usually indicates that the material in question has been either levigated, ground or burnt— in short, put through some kind of preparatory treatment—and is therefore in frequent use for all the colours.

Barium sulphate :

Heavy spar; barytes; heavy earth; mineral white.

Precipitated colours :

Permanent white; blanc fixe.

Yellow Earth Colours

Ferric hydroxide, with admixtures of ferric oxide, clay, lime, ferric silicate, basic ferric sulphate, etc.

Ochre; iron ochre; golden ochre; satin ochre (satinober); pit ochre; vitriol ochre; Mars yellow; Chinese yellow; Imperial yellow; permanent yellow; terra di Siena; umber; Italian earth; Roman earth; bronze ochre; oxide yellow, etc.

Yellow ochre; Jaune de Mars; Terre d'Italie.

Ferric Silicate :
Yellow earth; Argile jaune; yellow wash.

Red Earth Colours

Ferric oxide (with alumina and silica).

Bolus; bole; Terra sigillata; Lemnos earth; red chalk; raddle; Striegau earth.

Ferric oxide :
Colcothar; English red; angel red; Pompeii red; Persian red; Indian red; Berlin red; Naples red; Nuremberg red; crocus; chemical red; Crocus Martis iron saffron; caput mortuum; raddle; rouge de fer; Rouge de Perse; Rouge des Indes; Rouge de Mars; Rouge d'Angleterre.

Brown Earth Colours

Ferric oxide :
Ferric hydroxide; Ferric silicate (conf. Yellow Earth Colours, which are often sold under the same

names as the browns. The paler kinds are usually called " pale " or " golden," such as pale ochre, golden ochre, etc.). Terra di Siena; burnt Siena; satinober; mahogany brown; Vandyke brown.

Ferric silicate, Clay :
Umber; umber brown; Roman earth; Roman umber; Turkish brown; Sicilian brown; Cyprus earth; chestnut brown; burnt umber; ombre; Terre d'ombre; Ombre brulée.

Organic decomposition products :
Cologne umber; Cologne earth; Cassel brown; Spanish brown; mahogany brown; Vandyke brown; brown carmine; Terre brun de Cologne; Brun de Cologne; Brun d'Espagne; Ombre de Cologne; Brun de Cassel; Terre d'Ombre; Cologne brown.

Asphaltum (mineral rosin) :
Asphaltum brown; bistre; earth brown; bitumen; pitch brown; Asphalte; Brun de bitume; Bitume.

GREEN EARTH COLOURS

Ferrous oxide with silica, alumina, lime, etc. :
Green earth; Verona green; Celadon green; Verona earth; Italian green; stone green; Bohemian earth; Cyprus earth; Tyrol green; permanent green; green ochre; Terre verte; Terre de Vérone; Vert d'Italie.

Cupric carbonate :
Malachite green; mountain green; Hungarian green; copper green; mineral green; Tyrolese green; shale green; Vert de montagne; Vert d'Hongrie.

BLUE EARTH COLOURS

Cupric carbonate :
Malachite blue; mountain blue; lazulite blue;
azure blue; mineral blue; copper blue; Hamburg
blue; English blue; Cendres bleues; Bleu d'azure;
Bleu de cuivre; Vert-de-gris bleu; blue verditer.

GREY EARTH COLOURS

Grey clay shale :
Mineral grey; silver grey; stone grey; slate grey.

BLACK EARTH COLOURS

Carbon :
Graphite; blacklead; plumbago; iron black.

Clay shale :
Black chalk; slate black; Spanish black; Spanish
chalk; oil black; Schiste noir; Noir d'Espagne.

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